Biomass Gasification: An Alternative Solution to Animal Waste Management

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BIOMASS GASIFICATION: AN ALTERNATIVE SOLUTION TO ANIMAL WASTE MANAGEMENT

by

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A DISSERTATION

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Doctor of Philosophy

Major: Engineering

Under the Supervision of Professor Milford A. Hanna

Lincoln, Nebraska

May, 2013

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University of Nebraska, 2013

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The overall goal of this research was to evaluate gasification of animal waste as an alternative manure management strategy, from the standpoints of syngas production and biochar application.

To meet the overall objective, the thermogravimetric characteristics of dairy manure, as a thermochemical conversion feedstock, were studied firstly. Then, gasification technology was applied to dairy manure and feedlot manure using a fluidized-bed laboratory-scale gasifier. In addition, biochar derived from the feedlot manure was examined for its effects on nutrient leaching as a soil amendment. Finally, a life cycle assessment was conducted to evaluate greenhouse gas emissions of two feedlot manure management systems (land application and gasification).

Results showed thermochemical reactions were determined mainly by temperature, and heating rate influenced the start and the end of the conversions. Also, influences of gasification parameters (temperature, equivalence ratio and steam to biomass ratio) on syngas composition and energy efficiency were carefully discussed. Lower heating values of the syngas from dairy manure and feedlot manure gasification were in the range of 2.0 to 4.7 MJ m^{-3}, and 3.0 to 5.2 MJ m^{-3}, respectively. Further,

feedlot manure-derived biochar showed the ability to retain water and NH_4^+-N as the soil amendment. From the life cycle assessment, the net greenhouse gas emissions in land application scenario and gasification scenarios were 119 and -643 kg CO_2-eq for one tonne of dry feedlot manure, respectively, indicating that gasification of feedlot manure is a potential technique to mitigate global warming effects.

Acknowledgement

I would like to express my heartfelt appreciations to my advisor Dr. Milford Hanna. I still remember the day when I received the acceptation letter from Dr. Hanna three years ago, I was excited but also nervous, because the future seemed full of unknown. Now that my Ph.D. is finished, thinking back the past years at UNL, it's clear the best decision I ever made was to work with Dr. Hanna. His expertise, insight, support and encouragement have helped me to finish my research successfully. I am so heartedly grateful to Dr. Hanna.

I would like to thank my co-advisor Dr. David Jones. His ideas, comments and knowledge have made this research possible. Also, his kindness and patience have made me feel that he is not only a good mentor but also a good friend. I also want to thank my other committee members, Dr. Kumar and Dr. Noureddini, for their guidance during my research and study. Dr. Noureddini, thanks for the ideas you have given me during graduate studies and qualification presentation. Dr. Kumar, thanks for the many useful suggestions on the gasification experiment.

I would like to acknowledge Mr. Terry Bartels, who has helped me build and operate the gasification system. Dr. Thippareddi, Mr. Robert Weber, Mr. Alan Boldt, Mr. Loren Isom, and Ms. Courtney Burr, thanks all for the assistance you have given me during my research.

I would like to thank all the staff and faculty members of the Department of BSE. In addition, I would like to thank my colleagues and friends at UNL, like Pratik Bhandari, Shujing Zhang, Fangxia Yang, Luan Pan, Tiantian Xu, Chao Tai, Bo Yuan, Denis Mutiibwa and many others.

Last but not the least; I am extremely indebted to my parents, Zehui Wu and Rui Chen. Without their support, I would never have come to the U.S. to do my Ph.D. and fulfill my dreams.

DISSERTATION FORMAT

This dissertation consists of seven chapters. Five of the seven chapters are intended for publications in scientific journals. Each of the five central chapters has its own introduction, methods, results, discussions, conclusions and references, which are formatted according to the journal for publication.

The first chapter is the introduction. Background information and objectives of this thesis are included in the first chapter. The second chapter investigates thermogravimetric characterization of dairy manure as pyrolysis and combustion feedstocks. Follow up, experimental studies on gasification of dairy manure and feedlot manure are included in chapters three and four, respectively. The fifth chapter deals with biochar effects on nitrogen and phosphorus leaching. Then, the sixth chapter evaluates greenhouse gas emissions of feedlot manure management practices (land application and gasification) by life cycle assessment. The seventh chapter is a summary of this dissertation and recommendations for future research regarding the gasification of animal waste.

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CHAPTER I

INTRODUCTION

The most common types of animal waste include manure, litters, composts and lagoon effluents. Historically, animal waste has been the primary source of plant nutrients for agriculture crop production, and the most common utilization method has been land application. However, millions of swine, poultry, and cattle are fed in concentrated animal feeding operations, resulting in enormous amounts of animal manure. Consequently, a series of environmental issues, such as the eutrophication of surface water, the fate of trace elements, pathogens and odorous compounds to the surroundings have forced us to reevaluate land application of animal wastes. Therefore, alternative strategies have been proposed by researchers to address environmental problems and utilize the energy and nutrients within animal waste. For example, anaerobic digestion, thermochemical conversion and bioethanol production are all possible solutions with different purposes. Thermochemical processing animal waste has the advantages of having a short conversion time, destroying pathogens and most pharmaceutically active compounds, and being adaptable to a variety of animal waste.

One thermochemical technology is biomass gasification, which is not a new technique, but rather dates back some 180 years, and now is attracting renewed interests due to the fossil fuel shortages and environmental concerns. The principle of biomass gasification is to produce syngas through thermal decompose of biomass, usually involving partial oxidation of the feedstock, in a reducing atmosphere of air, oxygen and/or steam. The syngas, composed mainly of CH_4, H_2, CO and CO_2, and its composition depends on a group of factors like biomass properties (moisture content, particle size, heating value, etc.), gasification agent (air, steam and oxygen) and operating conditions (temperature, equivalence ratio, etc.). The syngas can be used to generate heat and power, or synthesize other chemicals and liquid fuels, determined, in part, by its quality.

Additionally, a major byproduct of gasification is biochar, which is mainly carbon. As a soil amendment, biochar has been shown to increase soil fertility by improving nutrient and water retention, lowering soil acidity and density, and increasing microbial activity. In addition, biochar application to the soil has been found to reduce greenhouse gases, together with its ability to store carbon, providing a potential tool to mitigate the global warming effects.

This dissertation focused on the evaluation of biomass gasification as a waste management tool from the aspect of syngas production and biochar application. From the perspective of syngas production from animal manure gasification, thermogravimetric characterization of animal manure as the thermochemical conversion feedstock was investigated firstly. Then, a detailed analyses of the gasification parameters on syngas composition and energy efficiency was conducted, guiding us the future end use of the syngas from animal waste as an energy source or producing other chemicals. From the perspective of biochar application, characteristics of biochar from manure gasification were analyzed, and impacts of biochar on nutrient (P and N) leaching also were investigated, allowing us to evaluate the value of biochar as a soil amendment. Finally, greenhouse gas emissions of feedlot manure gasification system were evaluated, providing more environmental knowledge of animal manure gasification. Two common animal waste, dairy manure and feedlot manure were used as gasification feedstocks in this research. These two types of animal waste are very typical, and are produced with huge amounts annually.

Overall, comprehensive research was carried out to evaluate biomass gasification as a waste management tool, with the specific objectives to:

1) determine the selected thermochemical properties of dairy manure and feedlot manure,
2) investigate effects of gasification parameters on syngas composition and energy efficiency for the dairy manure and feedlot manure gasification,
3) examine impacts of biochar derived from feedlot manure on soil nutrient leaching, and
4) determine greenhouse gas emissions of feedlot manure gasification system, and compare it to the land application system by life cycle assessment.

CHAPTER II

THERMOGRAVIMETRIC CHARACTERIZATION OF DAIRY MANURE AS PYROLYSIS AND COMBUSTION FEEDSTOCKS

This research paper was published as Hanjing Wu, Milford A. Hanna and David D. Jones. Thermogravimetric characterization of dairy manure as pyrolysis and combustion feedstocks. *Waste Management & Research* 30:10 (2012), pp. 1066-1071

Abstract

Thermogravimetric analysis was used to examine the thermal behavior of dairy manure as a pyrolysis and combustion feedstock. Nitrogen and air were used as purging gases to analyze the pyrolysis and combustion reactions, respectively, and heating rates of 20^{o}C min^{-1}, 40^{o}C min^{-1} and 60^{o}C min^{-1} were applied. An Arrhenius model was used to estimate the kinetic parameters (activation energy, reaction order and pre-exponential factor). Results showed four steps for both the pyrolysis and the combustion reactions, with the second step being the most critical one and during which most thermal decomposition of cellulose, hemicelluloses, starch and protein occurred. Thermochemical reactions were determined mainly by temperature. Heating rate influenced the start and the end of the thermal conversions. The activation energies for the two major reaction zones were 93.63 kJ mol^{-1} and 84.53 kJ mol^{-1} for pyrolysis, and 83.03 kJ mol^{-1} and 55.65 kJ mol^{-1} for combustion. Knowledge of the thermal behavior of dairy manure provides guidelines for future energy utilization.

Key words: TGA, pyrolysis, combustion, dairy manure, kinetic model

1. Introduction

1.1 Animal Waste

In the United States, more than 500 million tonnes of manure are produced by 238,000 animal feeding operations (AFOs) every year. AFOs produce about 100 times as much manure as municipal wastewater treatment plants produce sewage sludge (Gerba and Smith, 2005; US Environmental Protection Agency, 2007). Historically, the primary use of animal manure has been land-applied fertilize due to its nutrient content. However, serious environmental problems result from excess land application of animal wastes, such as nitrogen and phosphorus runoff, greenhouse gases emissions, and the presence of trace metal (copper, zinc and arsenic) (Sanchez et al., 2009).

Therefore, alternative strategies are needed for animal waste management. Three possible solutions to extract renewable energy from animal waste are thermochemical, biochemical and physicochemical pathways (Huang et al., 2011). Thermochemical technologies can be divided further into combustion, pyrolysis, and gasification. Combustion is the conversion of chemical energy into heat with CO_2 and H_2O as byproducts, and it may have very significant benefits in reducing the volume of waste and producing energy (Sanchez et al., 2009). Pyrolysis is the thermal decomposition of biomass in the absence of O_2. Gasification falls between complete combustion and pyrolysis (Ro et al., 2009; Wang et al., 2011; Mansaray and Ghaly, 1999).

1.2 Thermogravimetric Analysis (TGA)

TGA is a highly precision method that studies the mechanism and kinetics of the thermal decomposition of biomass. It can be performed under isothermal conditions or non-isothermal conditions and allows for the estimation of kinetic parameters for various decomposition reactions (Seo, et al. 2010; Deng et al., 2008; and Damartzis et al., 2011). Understanding thermal degradation characteristics is crucial in the selecting, design and optimization of thermochemical conversion units and TGA has been applied widely for this purpose (Wang et al., 2011).

Previously, research has been carried out to analyze the thermal characteristics of waste from domestic, industrial and agricultural activities as an energy feedstock, including sewage sludge, cattle manure, swine solids and municipal solid waste (Otero et al. 2010;

Ro et al., 2009; and Peng et al., 2001). However, only a few researchers have used dairy waste as a thermochemical conversion feedstock. For instance, thermochemical conversion of dairy-manure based biomass through direct combustion was analyzed by Carlin et al., (2007). Mountains of dairy manure are generated annually, and the estimated dairy cow manure production in the U.S. was close to 200 million tonnes in 2007 (Gerber et al., 2010). In a dairy farm with 2,500 cows, as much waste as a city with 411,000 residents is produced (US Environmental Protection Agency, 2004).

The main objective of this research was to provide detailed information about the pyrolysis and combustion characteristics of dairy manure, as well as to study the influence of heating rate during TGA. Also, the kinetic parameters of the primary reactions in thermochemical conversion were obtained through a kinetic model. Above information will give the fundamental knowledge of dairy manure pyrolysis and combustion, and a general idea of thermochemical converting dairy waste to an energy source.

2. Methods

2.1 Materials and Equipment

Dairy manure samples, collected from the University of Nebraska Agricultural Research and Development Center (ARDC), were used as the raw material. Moisture content of initial collected dairy manure was more than 50%. During pretreatment, samples were dried, ground and sieved. The particle size of the manure sample was less than 0.5 mm. Ultimate analyses and moisture content of the manure sample were conducted by Twin Ports Testing, Inc. (Superior, WI, USA). Oxygen bomb calorimetry (Model: 1241, Parr Instrument, Moline, IL) was used to measure the energy content of the manure samples.

TGA were performed with a STA 6000 Simultaneous Thermal Analyzer (PerkinElmer Inc., Waltham, MA, USA).

2.2 Experimental Procedure

For each experimental run, a 10-30 mg manure sample was put in the microbalance of the TGA analyzer. N_2 and air (79% N_2 and 21% O_2) were used as the purging gases, each with a flow rate of 20 ml min^{-1}. The temperature of the samples was increased from 25^{o}C to 850^{o}C at heating rates of 20, 40 and 60 ^{o}C min^{-1}. Sample was held at 25^{o}C for 1 min, heated to 850^{o}C at the respective temperature scan rates and then held at 850^{o}C for 1 min. After the heating processes, the sample was cooled to room temperature. The thermogravimetry (TG) profile was used to determine the percentage of weight loss of the sample and the differential thermogravimetry (DTG) curve, obtained from the first derivatives of TG curve, was the rate of the weight loss (Wu et al., 2011). To check the repeatability, the experiment was conducted again, and the DTG and TG curves obtained were almost identical.

2.3 Kinetic Model

Thermal degradation of biomass is a complex process due to differences in the chemical composition of components within the biomass material. Partially overlapping peaks are observed frequently in mass loss rate curves, and different mathematical models have been developed for the thermal kinetics (Damartzis et al., 2011). In this project, a technique based on the Arrhenius equation was used to define the kinetic model (Mansaray and Ghaly, 1999).

The rate of the reaction was expressed as

$$-r = \frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where α was the conversion of the sample (α =(m_0-m)/(m-m_f) and where m_0, m_f and m were the initial, final and time-dependant mass of sample, respectively) (Huang et al., 2011), t was the reaction time elapsed, and n was the reaction order. The reaction rate *k* was determined by the following equation (Jiang et al., 2010).

$$k = Ae^{-\frac{E}{RT}} \quad (2)$$

where A was the pre-exponential factor, T was the absolute temperature, R was the universal gas constant and E was the activation energy. Combining Eqs. (1) and (2), and taking the natural logarithm yielded Equation (3) (Mansaray and Ghaly, 1999 and Font-Palma, 2012).

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1-\alpha) - \frac{E}{RT} \quad (3)$$

From this equation, the kinetic parameters (A, E and n) were obtained by multiple linear regression (Domínguez et al., 2008) using the SAS 9.2 statistical software (SAS Institute Inc., Cary, NC, USA).

3. Results and Discussions

3.1 Characteristics of Dairy Manure

Table 1 contains the characteristics of dairy manure. Dairy manure has a relatively higher ash content and lower energy content when compared to other biomass materials. For example, the ash content and energy value of corn stalks are 8.18% and 18.45 MJ kg^{-1} (Kumar et al., 2008), and for rapeseed stalks are 5.87% and 17.67 MJ kg^{-1}

(Karaosmanoğlu et al., 2001). The composition of dairy manure is indicated in Table 2, which shows dairy manure to be a very complicated feedstock with a wide range of constituents. Cellulose is the major component, followed by protein, starch, lignin and hemicelluloses. On the other hand, the weight fraction of cellulose of the woody biomass is in the range of 40% to 50% (McKendry, 2002). Selection of biomass conversion technology is determined mainly by the components of the biomass. For example, ash, alkali and trace contents have the adverse effects on thermal conversion process, and the cellulose content influences biochemical fermentation process (McKendry, 2002).

3.2 Pyrolysis Characteristics

TG and DTG curves for the 20°C min^{-1} heating rate under a N_2 atmosphere are shown in Figure 1. The profile of dairy manure weight loss exhibited four stages during the degradation process (Figure 1). During the first stage (from room temperature to around 160°C), the weight loss was 10% -12% of the original weight. The moisture content of the dried manure sample was approximately 8% as shown in Table 1. Therefore, although volatile compounds may have contributed to the weight loss, the major weight loss was mainly due to the evaporation of moisture during the stage I (Liu et al., 2009).

The weight loss between the temperatures of 160 and 600°C was the major reaction area where most of the organic matter was lost. Since two dips in the DTG curve were observed, this reaction zone was divided into additional two stages (stage II and stage III). In the second stage (160 -360°C), around 35% of the original weight was lost. A sharp weight loss was observed in this stage, and the highest weight loss rate was reached at the temperature of 290°C. Consequently, the second stage was considered to be the critical stage in the pyrolysis process (Domínguez, et al., 2008). The weight loss during this stage results mainly from the thermal degradation of cellulose, hemicelluloses, protein, starch and microbial cell walls (Wu et al., 2011). For the third stage (360 - 600^{o}C), the mass loss rate was slower than for the second zone, and about 27% of the original weight was lost. Lignin in dairy manure may contribute to this weight loss (Wu et al., 2011) because the pyrolytic decomposition of lignin occurs between 300 and 500^{o}C. Hemicellulose decomposes at 250 - 300^{o}C and cellulose at 300 to 350^{o}C (Carrier et al., 2011). Most of the starch and protein were lost during the second stage. The thermal degradation of lignin was reported to be slow and over a wide range (up to 900^{o}C) (Huang et al., 2011), which may have been due to the extremely wide temperature range of the activity of chemical bonds and functional groups in lignin (Wang et al., 2009). The 6% weight loss during stage VI (600 - 850 ^{o}C) may have contributed to further charcoal devolatilization (Font-Palma, 2012). In the last stage, the weight loss rate became stable and near zero. The remaining solid residue at the end of pyrolysis was char (including ash and fixed carbon), which was 21% of the original mass. The ash content from Table 1 was 23.89% higher than the pyrolysis residue content, and two reasons may explain above phenomenon. The first is the variety of the manure samples and the second is the traces of oxygen remaining in the thermal analyzer before experiment operation.

3.3 Combustion Characteristics

TG and DTG curves for dairy manure oxidized in air with a heating rate of 20^{o}C min^{-1} are shown in Figure 2. In combustion reactions, the air was sufficient for complete combustion. Similar to pyrolysis, four stages were observed. The first stage (from room temperature to 165^{o}C) mainly resulted from the evaporation of water (11% weight lost). The second oxidation zone, which was the most significant zone, ranged from 165 to

360^oC, and around 34% of the original mass was lost. The highest weight loss rate was observed at 300^oC (the sharpest peak), which was a little higher than the temperature with the maximum weight loss rate during pyrolysis. Analogous to pyrolysis, weight loss in the second zone resulted from combustion of cellulose, hemicelluloses, protein and starch. The third oxidation zone which started at 360^oC and ended at 590^oC, may have been due to the lignin oxidation (Wang et al., 2011). The fourth oxidization zone may be explained by the further oxidization of char. The weight loss rate was slow with only 3% of the original weight being lost. At the end of the combustion, the remaining solid was ash, with a weight of about 19% of the initial weight.

3.4 Influence of Heating Rate

The influence of heating rate on TG curves under atmospheres of N_2 and air, respectively are shown in Figures 3a and 3b. In addition, influences of heating rate on DTG curves are shown in Figure 4.

It can be seen from Figure 3 that the final residue weight increased with higher heating rate. That may have been caused by insufficient time for the reaction to complete at the higher heating rates (Karaosmanoğlu et al., 2001). Additionally, when the heating rate increased, the starting and ending temperatures of pyrolysis and combustion increased (Figure 3).

In Figure 4, the peaks in the DTG curves shifted to higher temperatures with higher heating rates. The above observations were the result of a serious thermal lag effect when the heat transfer rate was low (Kumar et al., 2008; Deng et al., 2008). At the same time, the TG curves were basically parallel, indicating a similar reaction mechanism at the different heating rates. Therefore, both pyrolysis and combustion were influenced mainly by reaction temperature (Zhang et al., 2006).

3.5 Reaction Kinetics

Usually kinetic analyses focus on the most severe stage of thermochemical reactions. The second and the third stages of pyrolysis and combustion were the two major reaction zones during which almost all thermal degradation occurred. Therefore, the kinetic parameters were defined for these two regions. Because TGA was much more precise at low heating rates (Varhegyi et al., 2011); an Arrhenius model was applied under the condition of $20^{o}C\ min^{-1}$. Kinetic parameters are shown in Table 3, where R^2 indicates the model fitness using multiple linear regression.

From Table 3, R^2 values ranged from 0.82 to 0.87, indicating relatively good fitness of the model. However, in order to find out the best kinetic model, other regression methods can be applied further for comparison (Haralampu et al., 1985). In addition, for pyrolysis, the activation energies were 93.63 kJ mol^{-1} and 84.53 kJ mol^{-1} for the second and the third regions, respectively. For combustion, the activation energies were 83.03 kJ mol^{-1} and 55.65 kJ mol^{-1} for the two major reaction regions, which were lower than pyrolysis. Activation energies in this study were consistent with the values reported by Ramiah (1970), who indicated that the activation energy for thermal degradation for cellulose, hemicellulose and lignin samples was in the range of 150-251, 63-109, and 54-79 kJ mol^{-1}, respectively. Also, the activation energies for the second step were higher than the third step for both pyrolysis and combustion, together with a higher reaction order. Generally, the larger the activation energy, the more difficult is the thermochemical conversion process signifying the second reaction zone was more complex and difficult than the third reaction zone (Zhang et al., 2006).

4. Conclusions

Thermal characteristics of dairy manure were studied using thermogravimetric analysis. Four reaction stages were observed for both pyrolysis and combustion of dairy manure. The second step was considered the critical stage, where the highest conversion rate was reached and the most volatiles released. From thermogravimetry and differential thermogravimetry curves, conclusions were drawn that pyrolysis and combustion were dependent mainly on reaction temperature. In addition, heating rate influenced the starting and ending points of the reactions, and the peaks in DTG curves shifted to high temperatures at higher heating rates.

Kinetic parameters also were estimated by a kinetic model based on the Arrhenius equation. Results showed that during pyrolysis, the activation energies were 93.63 kJ mol^{-1} and 84.53 kJ mol^{-1} for the two major reaction zones, respectively. During combustion, the activation energies were 83.03 kJ mol^{-1} and 55.65 kJ mol^{-1} for the second and third steps.

Our experimental data provides basic information on dairy manure as pyrolysis and combustion feedstocks. The thermal characteristics will be a useful in guiding thermochemical conversion applications.

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Table 1. Characteristics of dairy manure

Moisture content (% wet basis)	7.78
Ultimate analysis (% wet basis)	
C	35.21
H	4.07
O	27.35
N	1.48
S	0.234
Ash	23.89
Higher heating value (MJ kg^{-1})	11.6

Table 2. Constituents of dairy manure

Component	% dry basis			
Volatile solids	83.0	85	83.0	89.9
Ether Extract	2.6	4	2.5-2.8	-
Cellulose	31.0	21	31	27.3
Hemicellulose	12.0	13	12	24.8
Lignin	12.2	10	12.2	18
Starch	12.5	-	-	-
Crude Protein	12.5	18	12.5	12.7
Ammonia	0.5	0.3	0.5	-
Acids	0.1	-	0.1	-
Reference	Stafford, 1980	Wohlt et al., 1990	Robbins et al., 1979	Jeyanayagam and Collins, 1984

Table 3. Kinetic parameters for pyrolysis and combustion of dairy manure

Pyrolysis				
Temperature range (°C)	A (min^{-1})	E ($kJ\ mol^{-1}$)	N	R^2
160-360 (Stage II)	4.22×10^8	93.63	6.37	0.83
360-600 (Stage III)	7.33×10^5	84.53	2.33	0.82
Combustion				
Temperature range (°C)	A (min^{-1})	E ($kJ\ mol^{-1}$)	N	R^2
164-360 (Stage II)	2.32×10^7	83.03	5.24	0.87
360-591(Stage III)	1.47×10^3	55.65	1.25	0.85

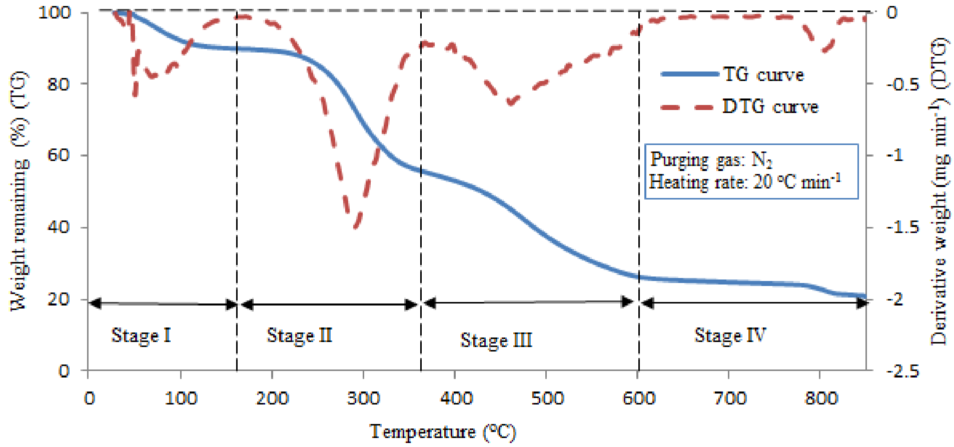

Figure 1. TG and DTG curves of dairy manure under N_2 with the heating rate of 20^{o}C min^{-1}

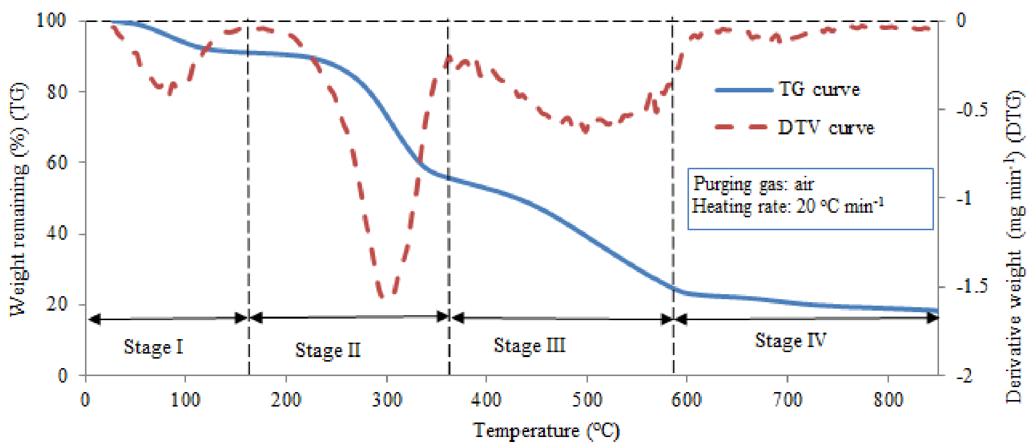

Figure 2. TG and DTG curves of dairy manure under air and with the heating rate of 20^{o}C min^{-1}

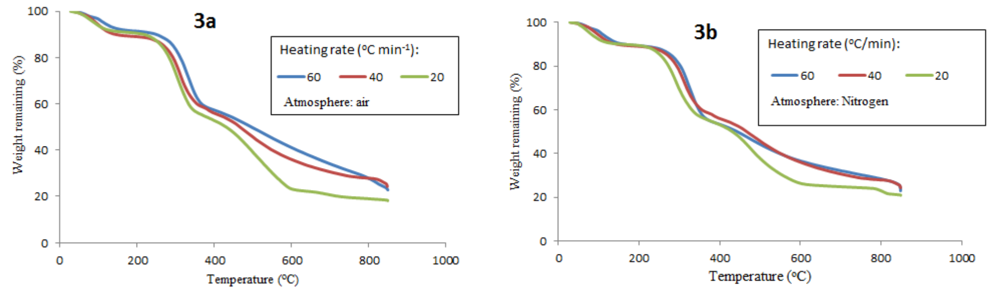

Figure 3. Influences of heating rate on TG curves under atmospheres of N_2 (3a) and air (3b)

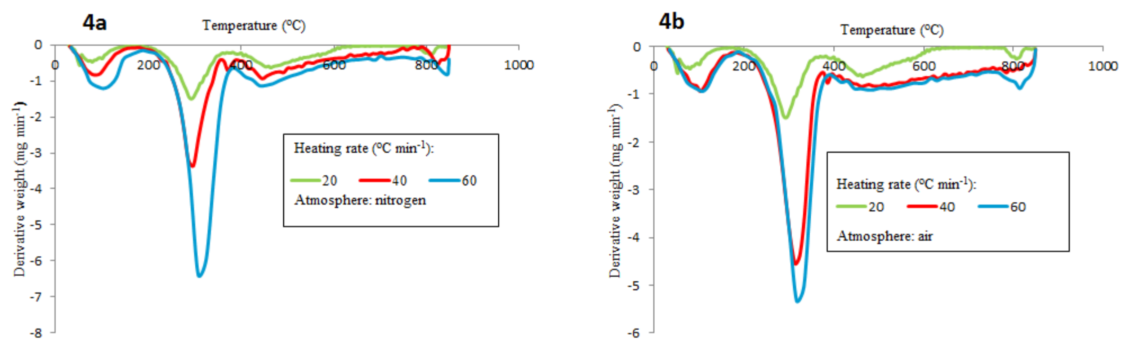

Figure 4. Influences of heating rate on DTG curves under atmospheres of N_2 (4a) and air (4b)

CHAPTER III

FLUIDIZED-BED GASIFICATION OF DAIRY MANURE BY BOX–BEHNKEN DESIGN

This research paper was published as Hanjing Wu, Milford A. Hanna and David D. Jones. Fluidized-bed gasification of dairy manure by Box–Behnken design. *Waste Management & Research* 30:5 (2012), pp. 506–511

Abstract

Land application of excessive animal manure may cause some environmental problems, such as eutrophication of surface waters, degradation of ground water quality, and threats to human health. This paper is an experimental study on the technology of biomass gasification to treat animal waste by analyzing effects of key operating parameters on gasification. In our research, dairy manure from the University of Nebraska dairy farm was first collected and dried, and then gasified in a fluidized-bed, laboratory-scaled gasifier to generate syngas. The effects of three parameters, i.e., temperature, steam to biomass ratio (SBR) and the equivalence ratio (ER), on the gasification were described by a Box-Behnken design (BBD). Results showed that increasing the temperature favored the formation of all three combustible gases, but the composition of each gas behaved differently according to the changing parameters. The lower heating value of the syngas varied from 2.0 to 4.7 MJ m^{-3}, indicating gasification could be used as a waste management option to produce bioenergy, and potentially reduce animal-waste disposal problems.

Key words: dairy manure, fluidized bed gasification, manure management, syngas production, Box-Behnken design

1. Introduction

Animal manure is a carbon-rich substance commonly applied to crop fields as a source of organic fertilizer, and according to an USDA estimation, more than 335 million tonnes of manure waste is produced annually on farms in the United States (USDA Agricultural Research Service, 2006). However, manure may be transported to surface water and groundwater through runoff and infiltration, when applied in amounts greater than can be used by the soil (Campagnolo et al., 2002). Consequently, some new technologies have been proposed to treat animal waste, and one of them is gasification. With the purpose of converting the manure waste into clean fuel gas, gasification technology has been taken into account by some researchers as an alternative way to treat animal wastes in nutrient and energy recovery strategies (Prapaspongsa et al., 2009).

The principle of biomass gasification is to produce syngas through the thermo chemical conversion of biomass, usually involving partial oxidation of the feedstock in a reducing atmosphere in the presence of air, oxygen and/or steam (Li et al., 2004). The composition of the syngas is the result of a combination of a series of chemical reactions. The main reactions are (Franco et al., 2003; Ciferno & Marano, 2002):

$$2C+O_2=2CO \tag{1}$$

$$C+O_2=CO_2 \tag{2}$$

$$C+2H_2=CH_4 \tag{3}$$

$$CO+H_2O=CO_2+H_2 \tag{4}$$

$$CO+3H_2=CH_4+H_2O \tag{5}$$

$$C+H_2O=CO+H_2 \tag{6}$$

$$C+CO_2=2CO \tag{7}$$

Previous work has been done to apply gasification to treat animal waste. For example, Gordillo & Annamalai (2010) studied adiabatic fixed bed gasification on dairy biomass with steam and air. Young & Pian (2003) investigated the feasibility of integrating an advanced gasifier into the operation of a dairy farm for converting biomass wastes into fuel gas that can be used for power production. Research into fixed-bed gasification of feedlot manure and poultry litter biomass was conducted by Priyadarsan et al. (2004). However, less detailed information has been provided about effects of operating conditions on syngas generated by animal manure. In this paper, dairy manure was gasified, and three key parameters were selected as the dependent variables: temperature, equivalence ratio (ER) and steam to biomass ratio (SBR). Though effects of some other parameters were analyzed in the previous gasification experiment, including the particle size of biomass and secondary air injection (Narvaez, et al., 1996, Lv et al. 2004, and Li et al., 2004), these three parameters were considered as the most important variables that influenced chemical reactions in the gasifier. Box-Behnken design (BBD) is a type of factional factorial designs, which is very efficient because of its smaller sample sizes (Haaland, 1989). Based on the principle of response surface methodology (RSM), BBD was applied to evaluate the effects of the above three factors on the syngas composition and energy efficiency of the gasification processes in this paper.

2. Material and Methods

2.1 Materials

Fresh dairy manure collected from the University of Nebraska dairy farm was dried in the oven (60^{o}C) for two weeks, and then ground. After that, the moisture content, heating value, particle size distribution and ultimate analysis were conducted on the dried manure.

2.2 Equipment

The fluidized-bed gasification system is shown in Figure 1. The gasifier had two parts. The length of the lower part (bed) was 700 mm with an inside diameter of 3.81 cm, and the length of the upper part (freeboard) was 500 mm with an inside diameter of 6.35 cm.

A data acquisition system (Model: NI SCXI-1102 with 32-channel thermocouple terminal block) and LabView 2009 (National Instruments Corporation, Austin, TX, USA) were applied to monitor the temperature at several locations throughout the gasification system.

2.3 Operation

At the beginning of the experiment, the fluidized bed was charged with 80 g of silica sand as the fluidized bed material, with the purpose of stabilizing fluidization and better heat transfer (Lv et al., 2003). The gasifier was heated by a tube furnace made of black iron, and the saturated steam was superheated. After both of the gasifier temperature and steam temperature reached their predetermined set points, air was fed into the gasifer first, and then the manure samples were fed at a constant rate of 1.67 kg hr^{-1}. After 2 to 3 min, when syngas was observed downstream, superheated steam was fed from the bottom of the gasifier. After another 5 min, syngas generated was collected in gas sample bags, and char was collected at the bottom of the cyclone separator (Kumar et al., 2009).

Gas Sampling and Analysis

For every experimental run, 4 sample bags were used. The composition of the syngas collected was analyzed by a gas chromatography system (Model: AutoSystem GC, PerkinElmer Inc., Waltham, MA). Since syngas contained very small amount of NH_3 and H_2S, the lower heating value (LHV) only took into account of CH_4, CO and H_2. This value was calculated by equation (8) (Kumar et al., 2009).

$$\text{LHV of syngas (MJ m}^{-3}\text{)} = (35.81\times CH_4+12.62\times CO+10.71\times H_2) \tag{8}$$

where CH_4, CO and H_2 were the volume fraction of each gas.

2.4 Experimental Design

Box-Behnken designs (BBD) are experimental designs for response surface methodology, which explores the relationships between several explanatory variables and one or more response variables (Zhu et al., 2010). BBD consists of a central point and the middle points of the edges of the cube circumscribed on the sphere (Kumar et al., 2008). These designs are rotatable (or near rotatable) and require 3 levels of each factor, and the geometry of a three factor BBD is shown in Figure 2 (Eriksson et al., 2008). In this experiment, a three-level three-factor BBD was applied to investigate the gasification parameters affecting the syngas composition and energy efficiency during the whole process. The three variables were temperature, ER and SBR, and the latter two were defined as follows (Lv et al., 2004).

$$ER=\frac{\text{weight air/weight dry biomass}}{\text{stoichiometric air/biomass ratio}} \quad (9)$$

$$SBR=\frac{\text{Weight of steam}}{\text{Weight of biomass}} \quad (10)$$

The response values were CH_4, CO, H_2, and energy efficiency, respectively; therefore, four models were established. Energy efficiency is defined by equation (11) (Rajvanshi, 1986).

$$\text{Energy efficiency}=\frac{\text{LHVgas}\times\text{F}}{\text{D}\times\text{E}} \quad (11)$$

where F was the flowrate of the syngas ($m^3\ min^{-1}$), LHV_{gas} was the lower heating value of the syngas ($MJ\ m^{-3}$), D was the flowrate of dairy manure ($kg\ min^{-1}$), E was the LHV of dairy manure ($MJ\ kg^{-1}$).

Three variables were equally spaced, and the low, middle, and high levels of each variable were coded as -1, 0, and 1, respectively, as given in Table 1. The experimental design is given in Table 2 (Annadurai & Sheeja, 1998; Kumar et al., 2007). For each experimental run, there were three replications.

2.5 Statistical Analysis

The statistical software SAS 9.2 (SAS Institute Inc., Cary, NC, USA) was used to establish the quadratic model, and the statistical software MINITAB 14.1 (Minitab Inc., PA, USA) was applied to define the response surface plots.

3. Results and Discussions

3.1 Characteristics of Dairy Manure

Characteristics of dairy manure, including moisture content, ultimate analysis, heating value and mean particle size are shown in Table 3.

3.2 LHV of Syngas

The LHV of the syngas generated by air and steam gasification of dairy manure ranged from 2.0 to 4.7 MJ m^{-3}, which was lower than that of the syngas produced through oxygen gasification (oxygen as the gasification medium), usually more than 10 MJ m^{-3}, due to nitrogen dilution (Ciferno & Marano, 2002). In addition, the value was lower than that of the syngas from pine sawdust (6.7 MJ m^{-3} to 9.1 MJ m^{-3}) (Lv et al., 2004) and olive particles (10.9 MJ m^{-3} to 13.1 MJ m^{-3}) (Rapagna et al., 2000), due to the relatively lower calorific value of dairy manure. However, this syngas can still be combusted to generate heat for steam or power generation (Priyadarsan et al., 2004), and Wang et al. (2009) pointed out that low heat-value syngas can be used in a combustor.

3.3 Char Content

Amount of char separated by the cyclone varied 5 - 35g in all experimental runs. As a byproduct of gasification, char was manufactured from biomass. Therefore char was high in carbon content and also contained a range of macro- and micro- nutrients (Lehmann & Joseph, 2009). In general, fluidized beds have high carbon conversion efficiencies (the percentage of carbon entering the gasifier that is converted into syngas), consequently, relatively fewer char was produced (Swanson et al., 2010).

3.4 Statistical Model

The four statistics models developed are listed in Table 4, where the coefficients of determination (R^2) indicate the overall fit of the model, and the square root of the variance of the residuals (RMSE) measure the difference between the predicated and the observed value.

3.5 CH_4 Production

The influences of two parameters on methane yield, while holding the third parameter at the middle value, are shown in Figure 3(a), 3(b) and 3(c). From the plot, it can be seen that the range of methane generated by dairy manure gasification varied from 2% to 8%. In 3(b) and 3(c), with increasing SBR, the methane yield decreased first until the value of SBR reached around 1.4, of which the methane yield became stable. On the other hand, temperature and ER did not significantly influence the methane yield. Similar results were reported by Narvaez et al. (1996), pointing out that CH_4 amount did not vary a lot when gasification temperature went up from 700^{o}C to 850 ^{o}C.

3.6 CO Production

The influences of two parameters on the CO yield, while holding the third parameter at the middle value, are shown in Figure 4(a), 4(b) and 4(c). During gasification of dairy manure, not much CO was produced, which may have been due to the relatively low energy density of dairy manure. The CO concentration decreased significantly with the decreasing SBR shown in 4(b) and 4(c), the same trend was observed by Franco et al. (2003). Besides, the declining ER resulted in a rising concentration of CO, which was explained by Turn et al. (1998) that as ER decreased, less fuel was converted into CO_2 and H_2O, and steam gasification (reaction (6)) became more important, producing more CO.

3.7 H_2 Production

The influences of two parameters on the H_2 yield, while holding the third parameter at the middle value, were shown in Figure 5(a), 5(b) and 5(c). From the plot 5(a) and 5(c), an increasing trend of H_2 concentration was observed when the gasification temperature was increased from 650 ^{o}C to 850 ^{o}C. In another aspect, with the SBR rising from 0 to 0.8, the H_2 concentration increased from 10% to 14%, after which, increasing SBR did not increase H_2 predication. It may be explained that for a SBR lower than 0.8, not enough steam reacted with all the biomass and reaction (4) (water-gas shift) and (6) (steam-carbon reaction) did not seem to reach a state of completion. Consequently, concentration of CO decreased, and the H_2 concentration increased simultaneously. With the increasing steam input, the influencing reactions could reach a state equilibrium, leading to the maximum value of H_2 yield (Franco et al. 2003).

3.8 Energy Efficiency

The influences of two parameters on the energy efficiency, while holding the third parameter at the middle value, are shown in Figure 6(a), 6(b) and 6(c). Energy conversion efficiency of gasification of dairy manure (15 % to 30 %) was lower than that of wood, which was about 60%-70% (Ciferno & Marano, 2002). It was interpreted that dairy manure had a relatively lower heating value than wood, and more ash content. It also showed that temperature was the most influential factor with respect to the energy efficiency. Higher temperature favored the higher energy efficiency.

4. Conclusions

1) Dairy manure was successfully gasified in a laboratory-scale fluidized-bed gasifier, and the syngas was sampled and analyzed. In addition, a three factorial BBD design was applied to evaluate three operating conditions (temperature, ER and SBR) on the syngas composition and energy efficiency of the gasification process.
2) The increasing temperature increased the combustible gas and energy efficiency on the whole; however, the composition of each gas also was determined by the comprehensive effect of all operating parameters. In general, an increasing SBR (0 to 0.8) led to a decreasing CH_4 concentration and an increasing H_2 concentration, and the declining ER (2.0 to 0) resulted in a rising concentration of CO.
3) Depending on the operating parameters, the LHV of the syngas varied from 2.0 to 4.7 MJ m^{-3}. Though it is a low-heating value gas, some end-use applications can

be taken into account. Experimental results suggest gasification could be used as a waste management option to reduce animal waste disposal problems in the U.S.

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Table 1. Level of three variables

Variables	Levels		
Coded level	-1	0	1
Temperature(^{o}C)	650	750	850
ER	0.08	0.14	0.20
SBR	0	0.88	1.76

Table 2. The three-level three-factorial Box-Behnken design

Exp No.	Temperature	ER	SBR
1	-1	-1	0
2	-1	1	0
3	1	-1	0
4	1	1	0
5	-1	0	-1
6	-1	0	1
7	1	0	-1
8	1	0	1
9	0	-1	-1
10	0	-1	1
11	0	1	-1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

Table 3. Properties of dried dairy manure sample

Moisture content (% wet basis)	7.78
Ultimate analysis (% wet basis)	
C	35.21
H	4.07
O	27.35
N	1.48
S	0.234
Ash	23.89
Higher Heating value (MJ kg^{-1})	11.6
Mean particle size (mm)	1.02

Table 4. Statistic model for each response value

Response value	Model	R^2	RMSE
CH_4	$y=3.39+1.10x_1-0.60x_2-1.55x_3-0.51x_1^2-0.028x_1x_2 +0.51x_2^2-0.33x_1x_3+0.30x_2x_3+1.65x_3^2$	86.0%	1.21
CO	$y=1.86+0.55x_1-0.49x_2-0.56x_3+0.025x_1^2-0.14x_1x_2-0.025x_2^2-0.060x_1x_3+0.12x_1x_2-0.083x_3^2$	97.0%	0.21
H_2	$y=12.03+1.11x_1-0.90x_2-0.90x_3+0.54x_1^2-0.26x_1x_2-0.47x_2^2+0.91x_1x_3-0.095x_2x_3-2.05x_3^2$	79.1%	1.53
Energy efficiency	$y=20.67+4.63x_1+2.13x_2-5.72x_3-0.97x_1^2-0.27x_1x_2+1.68x_2^2-2.075x_2x_3-0.37x_3^2$	94.1%	2.52

Note: x_1, x_2 and x_3 are the coded value for temperature, ER and SBR, respectively (from Table 1); All of x_1, x_2 and x_3 are in the range of [-1, 1].

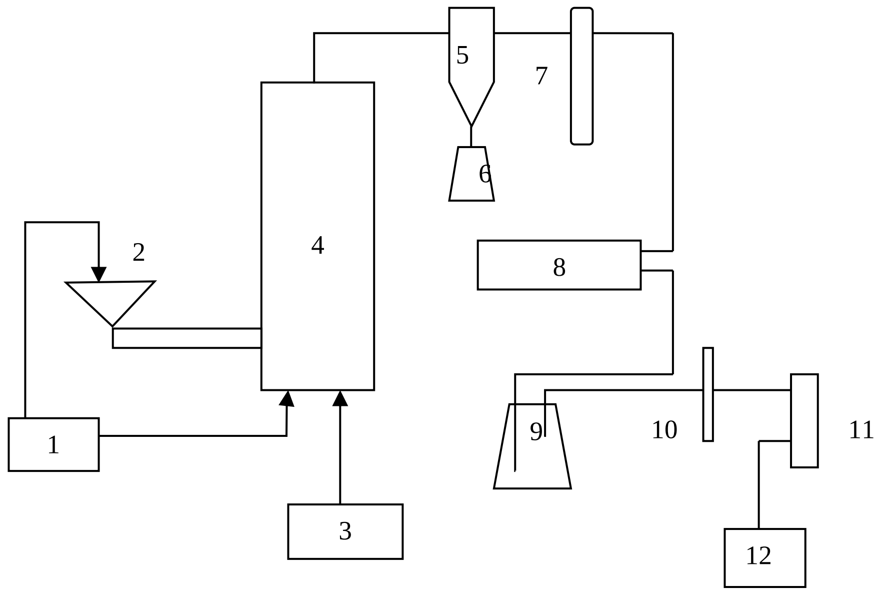

Figure 1. Schematic diagram of the fluidized-bed gasification system

(1-air supply system; 2-biomass feeder; 3-steam generator; 4-fluidized-bed gasifier; 5-cyclone separator; 6-char collection vessel; 7-high temperature filter; 8-heat exchanger; 9 condensation collection vessel; 10 syngas filter; 11-desiccator; 12-gas collection bag)

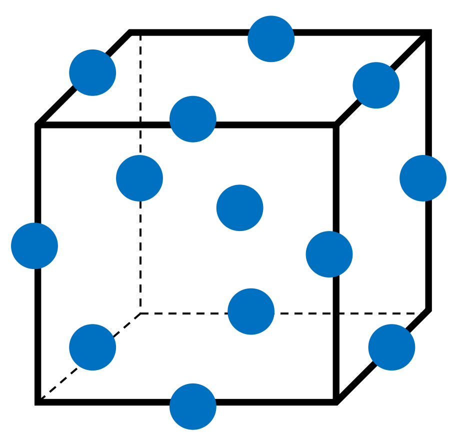

Figure 2.Geometry of a three factor BBD desing

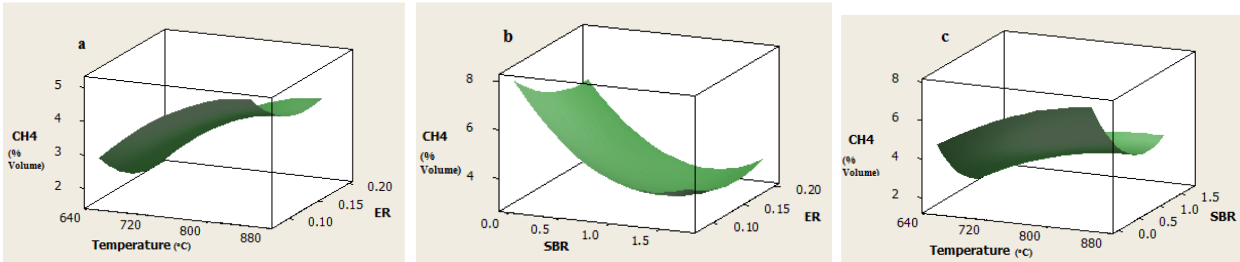

Figure 3. Influences of two parameters on CH_4 yield, where in (a) SBR=0.88, in (b) T=750^{o}C, and in (c) ER=0.14

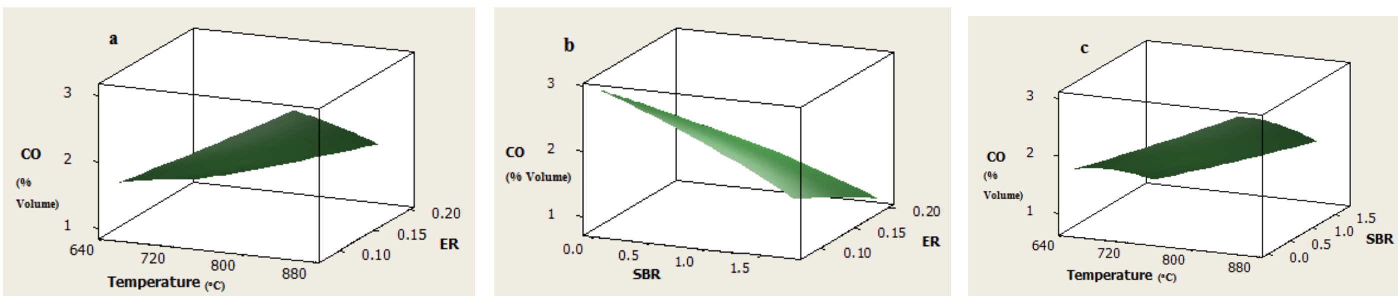

Figure 4. Influences of two parameters on CO yield, where in (a) SBR=0.88, in (b) T=750^{o}C, and in (c) ER=0.14

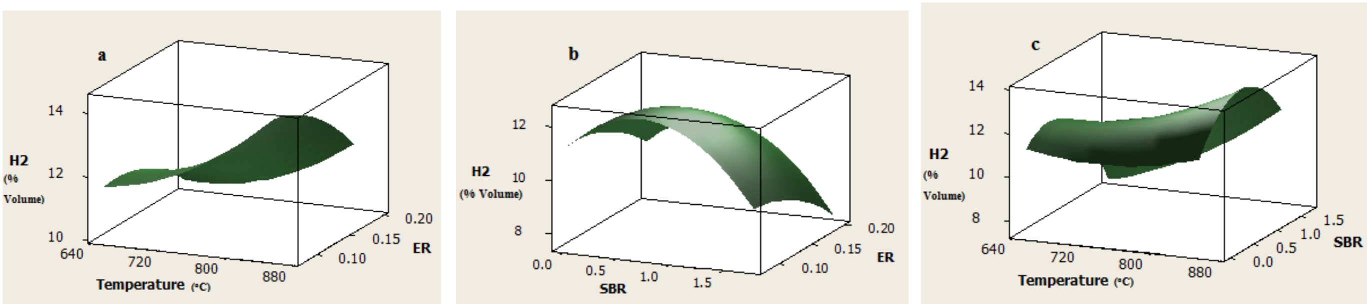

Figure 5. Influences of two parameters on H_2 yield, where in (a) SBR=0.88, in (b) T=750^oC, and in (c) ER=0.14

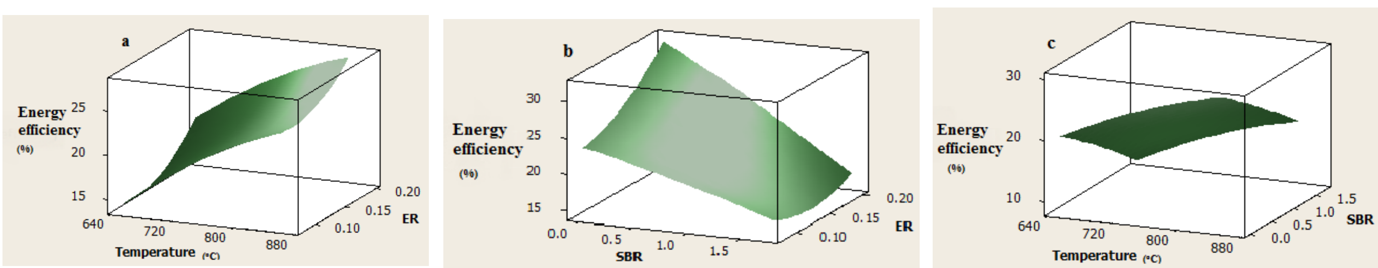

Figure 6. Influences of two parameters on energy efficiency, where in (a) SBR=0.88, in (b) T=750^oC, and in (c) ER=0.14

CHAPTER IV

OPTIMIZATION OF ENERGY EFFICIENCY FOR THE GASIFICATION OF FEEDLOT MANURE USING RESPONSE SURFACE METHODOLOGY

This research paper is intended to be published as Hanjing Wu, Milford A. Hanna and David D. Jones. 2012. Optimization of energy efficiency for the gasification of feedlot manure using response surface methodology.

Abstract

Large quantities of animal waste are produced annually. Alternative technologies are needed to treat animal waste for energy and nutrient recovery and also to avoid possible environmental pollution by land application. Gasification is a potential way to manage animal waste, with the goal of converting animal waste into useful energy - syngas. In this project, feedlot manure was gasified in a laboratory-scale fluidized-bed gasifier, with the objectives being to analyze gasification parameters on syngas composition and to optimize energy efficiency. A full factorial experiment was designed and conducted. The parameters were gasifier temperature (T), equivalence ratio (ER) and steam to biomass ratio (SBR). Results showed that T increased both CO and H_2 contents in our experimental range, but CH_4 concentration was reduced when T increased from 750^oC to 850^oC. With increasing SBR, there was an obvious ascending trend for H_2 production, but its formation reached a maximum when SBR was around 0.8. Increasing ER can result in the conversion of CO to CO_2, leading to a CO concentration drop. Energy efficiency was improved by higher T and ER, but more steam injection caused a drop in energy efficiency due to the relatively lower temperature of the superheated steam. Energy efficiency was optimized by a ridge max analysis. The optimum energy efficiency was 40%, when the temperature was 789 ^oC, ER was 0.20, and SBR was 0.50.

Kew words: Gasification, feedlot manure, energy efficiency optimization, response surface methodology (RSM)

1. Introduction

Large confinement facilities began to dominate livestock and poultry production in the U.S. a few decades ago (MacDonald and McBride, 2009; Walker et al., 2005). Therefore, not only the number of animals per facility increased significantly, but also huge quantities of manure, wastewater and bedding materials were produced (Cantrell et al., 2007).

Traditionally, the most common method to dispose of animal manure has been land application. Since most manure is applied directly and close to the source, its application at high rates leads to degradation of soil, water and air quality (Larney and Hao, 2007). Composting is another common and useful method to manage animal waste, with the advantages of little odor and reduced fly breeding potential during storage and spreading. Nevertheless, similar to land application, the nutrient loss during decomposition can cause environmental problems (Eghball, 2000). On the other hand, animal waste has great potential in terms of being converted into renewable energy through biological and thermochemical processes (He et al., 2000). Thermochemical conversation technology usually refers to combustion, pyrolysis and gasification.

Gasification technology is regarded as one of the most technically and economically convincing energy possibilities in a renewable energy economy, due to its ability to handle a wide range of biomass materials (Speight, 2008). Wood, soybeans, sawdust, corn stover, and municipal solid waste are all common raw materials for biomass gasification. During gasification, the feedstock is converted into syngas and biochar, with a temperature usually higher than 500 ^{o}C. The syngas is composed of combustible gases, such as CH_4, H_2 and CO, with composition being determined mainly by feedstock characteristics and operating conditions.

Using gasification to process animal waste has been attempted. For example, co-gasification of blended coal with feedlot and chicken litter biomass was examined by

Priyadarsan et al. (2004) and air-blown gasification of dairy-farm wastes was investigated by Young and Pian (2003). Advantages of applying gasification to animal wastes have been pointed out by Cantrell et al. (2007) as: (1) it has a very short conversion time when compared with anaerobic digestion; (2) the high temperature destroys pathogens and most pharmaceutically active compounds; (3) it is adaptable to a variety of animal manure feedstocks; and (4), there are no fugitive gas emissions.

In the United States, there are about 10 million head of cattle in feedlots which are producing harvestable manure (Priyadarsan et al., 2004). Appropriately managing cattle feedlot manure is crucial for energy production, nutrient recovery and environment protection. In this research, feedlot manure was gasified in a laboratory-scale fluidized-bed gasifer. The objectives were to better understand the relationships between gasification variables and responses (gas composition and energy efficiency) and to obtain the optimum conditions for energy efficiency by response surface methodology (RSM) analysis. The variables used in this study were gasifier temperature (T), equivalence ratio (ER) and steam to biomass ratio (SBR). ER is defined as the ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio, and SBR is the mass ratio of steam to biomass.

2. Materials and Methods

2.1 Feedlot Manure

Cattle feedlot manure was obtained from the Department of Animal Science, University of Nebraska-Lincoln. Fresh manure was dried in the drying room at the temperature of 60 ^{o}C. Manure samples were ground and then sieved to obtain a particle size less than 2.36 mm. Ultimate analyses and moisture content determination were conducted by Twin

Ports Testing, Inc. (Superior, WI, USA). Oxygen bomb calorimetry (Model: 1241; Parr Instrument, Moline, IL, USA) was used to measure the energy content of the manure samples.

2.2 Fluidized-bed Gasifer

A laboratory-scale fluidized-bed gasifier was used in this research. Detailed information about components and construction of the gasifer were presented in previous papers (Kumar et al, 2009; Wu et al., 2012). The advantage of a fluidized-bed gasifer is its flexibility to changes in moisture and ash contents, as well as its ability to deal with fluffy and fine-grained materials (Stassen et al., 1999).

2.3 Operation

Before gasification, the fluidized-bed gasifier was heated by an external furnace to reach the set temperature. Air and steam were preheated to 400 ^{o}C and 300 ^{o}C, respectively, before both of which were introduced into the gasifier. Also, 80g of sand were introduced into the gasifier to maintain the state of suspension before the biomass was fed in. The feeding rate of manure samples was set at 1.3 kg h^{-1}. Before collecting the syngas downstream, tar was removed by a filter and the syngas was dried by a desiccant. Biochar was collected at the bottom of the cyclone separator, and the final syngas product was analyzed by gas chromatography (Model: AutoSystem GC, PerkinElmer Inc., Waltham, MA, USA) for its composition. After each experimental run, the bottom of the gasifier was cleaned before the next run. The lower heating value (LHV) of the syngas was calculated by equation (1) (Wu et al., 2012):

$$\text{LHV of syngas (MJ m}^{-3}\text{)} = (35.81 \times CH_4 + 12.62 \times CO + 10.71 \times H_2) \quad (1)$$

where CH_4, CO and H_2 were the volume compositions of the respective gases. Energy efficiency (hot gas efficiency) was defined as the ratio of the sum of sensible and chemical energy content of the syngas to the lower heating value of the feedlot manure (Kumar et al., 2010).

2.4 Experimental Design

A full factorial design, as shown in Table 2, consisting of three factors each at three levels, was used in this research. There were three replications for each factorial combination. Therefore, 81 (3×3×3×3) gasification runs were conducted in total.

2.5 Statistical Analysis

Quadratic response surface regression models were used to fit gas composition and energy efficiency by PROC RSREG procedure in software SAS 9.2 (SAS Institute Inc., Cary, NC, USA). The four responses were the compositions of CH_4, CO and H_2 and energy efficiency. For each response variable, the model was (Lee et al., 2000):

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \qquad (2)$$

where y was the response and X_i were three factor variables shown in Table 2. β_0, β_i, β_{ii}, and β_{ij} were constant variables. Four models were established and then analyzed for lack of fit, which was used to compare the variation around the model with pure variation within replicated experiments (SAS, 2009). To optimize energy efficiency, a canonical analysis was used to investigate the shape of the predicted response surface. If the response surface was a saddle, ridge analysis was applied to search for the region of optimum response (SAS, 2009). 3-D response surface plots were drawn by the software Design-Expert version 7.1.6 (Stat-Ease Inc., Minneapolis, MN, USA).

3. Results and Discussions

3.1 Characteristics of Feedlot Manure

In general, the characteristics of animal waste biomass vary according to its original source, production conditions and collection sites. Also, biomass derived from animal waste differs significantly from woody or herbaceous biomass in the amount of chlorine and alkali compounds present (Santoianni et al., 2008). Table 1 shows the characteristics of the beef cattle feedlot manure used in this study, which was considered as excreted manure. The ash content was close to 10%, lower than that of harvest beef cattle manure exposed to the soil for a long time.

3.2 Model Fitting

Four quadratic response surface regression models were developed to estimate gas compositions and energy efficiency and are shown in Table 3. Also included are coefficients of determination (R^2) and lack of fit test results. Except for the model to estimate CH_4 composition, the models had satisfactory R^2 values. In addition, all four models showed insignificant lack of fit, indicating the models adequately represented the experimental data.

3.3 Lower Heating Value of Syngas

LHV of the syngas produced from gasification of feedlot manure varied from 3.0 to 5.2 MJ m^{-3}. The value was lower than those reported for syngas from pine sawdust (7.3-10.6 MJ m^{-3}) (Baratieri et al., 2008) and dried distillers grains (10.65 MJ m^{-3}) (Tavasoli et al., 2009), but higher than that from bluegrass straw (1.27 to 2.85 MJ m^{-3}) (Boateng et al., 2007).

3.4 Gas Composition Analysis

Although there is considerable overlap, the gasification process can be divided into four steps: drying, pyrolysis, combustion and reduction. During the drying process, the water contained in manure was evaporated, and during pyrolysis the dried manure decomposed into tar, char and low molecular gases. Because air was introduced into the gasifier, char and tar were partially oxidized to produce heat and CO_2 (Loo and Koppejan, 2008). The reduction step was when the major chemical reactions occurred in the gasifier and included five major reactions (Shen et al., 2008):

Water-gas reaction: $C + H_2O \rightarrow CO + H_2$ + 131.5 kJ/mol (3)

Boudouard reaction: $CO_2 + C \rightarrow 2CO$ +172.6 kJ/mol (4)

Water shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$ - 41.2 kJ/mol (5)

Methane production reaction: $C + 2H_2 \rightarrow CH_4$ -74.8 kJ/mol (6)

Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$ +206 KJ/mol (7)

Effects of T and SBR, when ER=1.6, and effects of ER and SBR, when T=750 ^oC, on CH_4 concentration are shown in Figure 1a and Figure 1b, respectively. Higher SBR decreased CH_4 content, which could have been a result of the steam reforming reaction (7). In addition, ER did not have obvious effects on CH_4 content. Also, when temperature increased from 650 ^oC to 750 ^oC, more CH_4 was produced. However, at even higher temperature (>750 ^oC) CH_4 concentration decreased slightly. From Fig. 1a, when SBR was 1.70 and ER was 0.16, CH_4 concentration dropped from 5.2% to 4.8% as temperature increased from 750 ^oC to 850 ^oC, and it could have been due to a contribution of reaction (7), shifted to the right with higher temperature (González et al., 2008). The above observation was in the agreement with conclusions made by Emami et al. (2012), that methane production was more dependent on gasifying agent (air and steam) than temperature. However, other researchers observed a more apparent drop in CH_4 concentration with higher temperatures. For example, CH_4 content dropped from 9.6% to 8.6% when temperature increased from 750 ^{o}C to 790 ^{o}C in in an allothermal fluidized bed gasifier (Mayerhofer et al., 2012).

Effects of T and SBR, when ER=1.6, and effects of ER and SBR, when T=750 ^{o}C, on CO composition are shown in Figure 2a and Figure 2b, respectively. For CO, all three factors influenced syngas composition significantly. Firstly, higher temperature produced more CO gas, which was the same conclusion made by Shen et al. (2008). According to Le Chatelier's principle, higher temperatures favored the reactants in exothermic reactions and favored the products in endothermic reactions (Lv et al., 2004). Therefore, in general, at higher temperatures, reactions (3) and (4) were strengthened, producing more CO. Secondly, when SBR was increased, the concentration of CO increased slightly. However, when the value of SBR approached 1, CO concentration dropped. That was because more steam injection favored the water shift reaction (7). From Fig. 2b, when T was 750 ^{o}C, higher ER decreased CO composition. That was because when more O_2 was introduced (higher ER), more CO may have been converted into CO_2. Similarly, Turn et al. (1998) indicated that CO composition decreased from 20% to 16% over the range of increasing ER (0 to 0.37) when sawdust gasification temperature was 850 ^{o}C. In addition, CO content was less than 4% in this research, which probably was due to the relatively lower temperature of our gasifier bed (around 400 ^{o}C) (Kumar et al., 2009).

Effects of temperature and SBR, when ER=1.6, and effects of ER and SBR, when T=750 ^{o}C, on H_2 composition are shown in Figure 3a and Figure 3b, respectively. Emami et al. (2012) pointed out that biomass gasification was the most efficient and economical route for H_2 production and the primary emphasis in biomass gasification was to maximize the contents of H_2. For H_2, T increased its composition significantly. It should be explained that reaction (7) was favored at higher temperature, leading to an increase of H_2 composition. This tendency (higher temperatures produced more H_2) also was reported by other researchers. For example, H_2 concentration increased from 32% to 41% when temperature increased from 700 to 850 ^{o}C during air gasification (González et al., 2008). Additionally, more steam produced more H_2 because more H_2O shifted the reaction (3) and (4) to the products, leading to enhanced formation of H_2 (Mayerhofer et al., 2012). However, higher values of SBR (>0.8) had the effect of reducing H_2 concentration. This result was similar to the conclusions made by Franco et al. (2003) that H_2 formation reached the maximum when SBR was in the range of 0.6 and 0.7, and H_2 concentration began to drop with even higher SBR. In our system, the temperature of superheated steam was relatively low (300 ^{o}C), injecting too much steam reduced operating temperature, which could lead to a lower H_2 concentration. When ER increased from 0.11 to 0.21, H_2 content gradually decreased. The same trend was reported by Lu et al. (2007), indicating that H_2 concentration decreased when ER increased from 0.0 to 0.5 with constant temperature and pressure. They suggested that to realize full self-heating of a biomass gasification system, larger ER was needed but may lead to even less H_2 production.

3.5 Energy Efficiency Optimization

Effects of T and SBR, when ER=1.6, and effects of ER and SBR, when T=750 ^{o}C, on energy efficiency are shown in Figure 4a and Figure 4b, respectively. Within our experimental range, both higher ER and T increased energy efficiency. Higher ER meant more O_2, and had an effect of accelerating thermochemical reactions and producing more syngas. When SBR increased from 0 to 0.5, energy efficiency did not change much. However, after that, energy efficiency gradually decreased with rising SBR. That may have been due to the relatively lower superheated steam temperature (300 ^{o}C), thus reducing the operation temperature. Therefore, higher SBR made the energy efficiency drop.

According to the canonical analysis within a SAS program, the optimization value was a saddle. Therefore, the optimum energy efficiency was determined by the ridge max analysis, which was used to compute the estimated ridge of optimum response for increasing radii from the center of original design (SAS, 2009). The maximum energy efficiency was 40%, when the temperature was 789 ^{o}C, ER was 0.20, and SBR was 0.50 at the distance of the coded radius 1.0.

3.6 Potential Problems

Gasification of animal manure not only produces renewable energy-syngas, but also the biochar produced can be used as the soil amendment. Biochar has been shown to reduce greenhouse gases, and a benefit to the environment (Lehmann and Joseph, 2009). However, several issues have to be addressed before its large scale application in industry. Firstly, during pretreatment, feedlot manure was dried in trays at 60^{o}C. Odor emission during the drying process was an environmental issue. Secondly, chunks of agglomerated deposits were observed at the bottom of the gasifier during the cleaning stage. The reason could have been the high content of alkali in the feedlot manure. Similar particle agglomeration observation was reported by Priyadarsan et al. (2004), during gasification of poultry litter biomass. Agglomeration of bed materials is a major problem in fluidized-bed gasifiers. Alkali salts in manure can react with silica in the sand to form a low-melting, eutectic mixture. This makes particle surface sticky and generates local hot spots, which leads to agglomeration and sintering (Basu, 2006). Thirdly, the LHV of the syngas from animal waste was relatively low when compared to syngas from other biomass materials.

4. Conclusions

In this research, a full factorial design was conducted on gasification of feedlot manure. The relationships between gasification variables and responses (gas composition and energy efficiency) were evaluated, and energy efficiency was optimized by ridge analysis in SAS. The conclusions follow:

Firstly, temperature increased both CO and H_2 contents, however, higher temperature (>750 ^oC) reduced CH_4 concentration, which may have been a result of steam reforming reaction. H_2 formation reached the maximum when SBR was around 0.8, however, even higher SBR had the effect of reducing H_2 concentration. In addition, with increasing ER, both CO and H_2 concentrations dropped, but ER did not have an obvious effect on CH_4 content.

Secondly, energy efficiency was improved by higher temperature and higher ER in our experimental range. Due to the relatively lower superheated steam temperature, too much steam reduced energy efficiency. According to the ridge max analysis, the optimum energy efficiency was 40%, when T was 789 ^{o}C, ER was 0.20, and SBR was 0.50.

Thirdly, gasification of feedlot manure still faces some challenges, i.e., odor emissions during drying process, agglomeration of bed materials and the relatively low heating value of syngas. These problems need to be addressed before its large-scale applications.

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Table 1. Characteristics of feedlot manure

Ultimate analysis (dry ash free basis %)	
C	55.9
H	8.06
N	4.48
O	30.9
S	0.690
Moisture content (wet basis %)	8.36
Ash (wet basis %)	11.0
Higher heating value (dry basis, Btu/lb)	7.87×10^3

Table 2. Experimental design

Factor	Actual value			Coded value		
	Low	Medium	High	Low	Medium	High
Temperature (^{o}C) (x_1)	650	750	850	-1	0	1
Steam to biomass ratio (x_2)	0	1.20	1.70	-1	0.412	1
Equivalence ratio (x_3)	0.11	0.16	0.21	-1	0	1

Table 3. Quadratic models for five response values with coded value

Response value	Quadratic model	R^2	Lack of fit
CH_4	$5.60+0.35x_1-0.81x_2-0.072x_3-0.11x_1x_2-0.34x_1x_3-0.027x_2x_3-0.12x_1^2+0.30x_2^2+0.097x_3^2$	0.63	Insigniciant
CO	$3.07+0.80x_1-0.27x_2-0.46x_3+0.024x_1x_2-0.32x_1x_3+0.15x_2x_3-0.19x_1^2-0.27x_2^2+0.041x_3^2$	0.86	Insigniciant
H_2	$10.64+1.11x_1+0.084x_2-0.10x_3+0.49x_1x_2-0.071x_1x_3-0.16x_2x_3+0.20x_1^2-0.89x_2^2+0.011x_3^2$	0.90	Insignificant
Energy efficiency	$0.33+0.037x_1-0.038x_2+0.069x_3+0.004x_1x_2-0.013x_1x_3-0.006x_2x_3+0.002x_1^2-0.024x_2^2-0.009x_3^2$	0.87	Insignificant

(Note: the coded values of x_1, x_2, and x_3 are shown in Table 2. Lack of fit P value>0.5 was considered insignificant.)

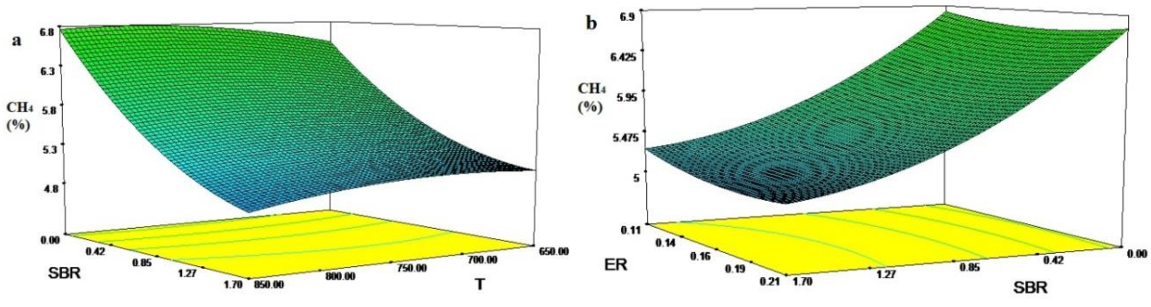

Figure 1. Effects of T and SBR on CH_4 content, when ER=1.6 (a), and effects of ER and SBR on CH_4 content, when T=750 ^oC (b)

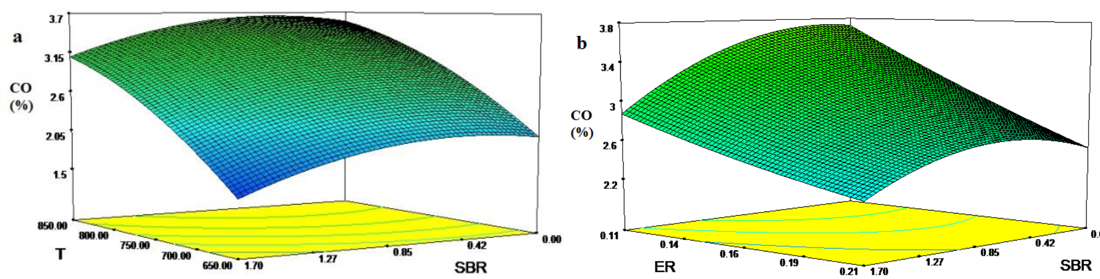

Figure 2. Effects of T and SBR on CO content, when ER=1.6 (a), and effects of ER and SBR on CO content, when T=750 ^oC (b)

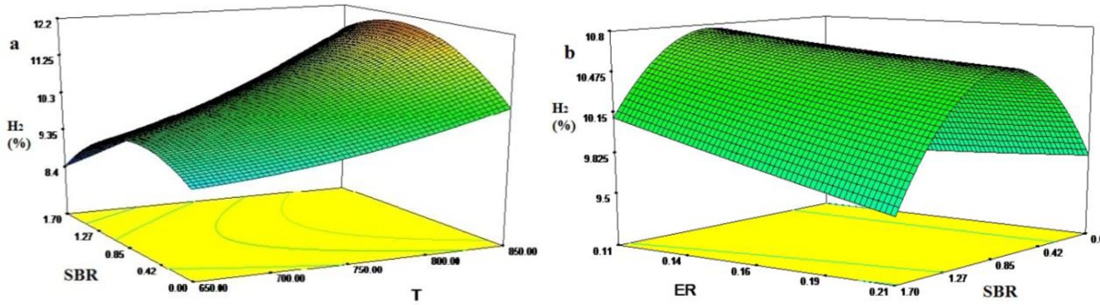

Figure 3. Effects of T and SBR on H_2 content, when ER=1.6 (a), and effects of ER and SBR on H_2 content, when T=750 ^oC (b)

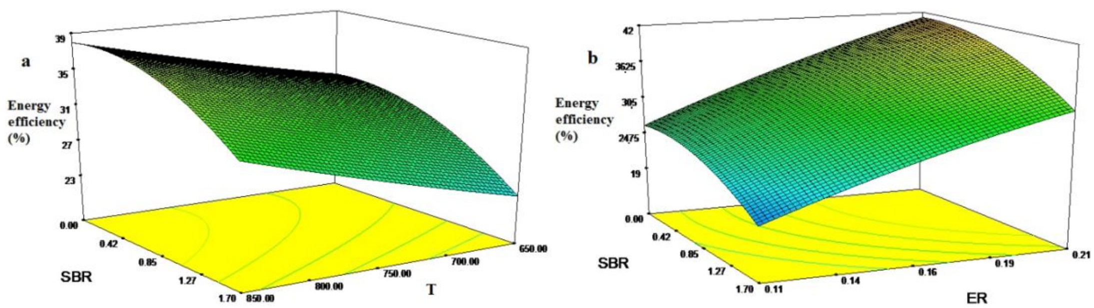

Figure 4. Effects of T and SBR on energy efficiency, when ER=1.6 (a), and effects of ER and SBR on energy efficiency, when T=750 ^oC (b)

CHAPTER V

FEEDLOT MANURE-DERIVED BIOCHAR EFFECTS ON NITROGEN AND PHOSPHORUS LEACHING

This research paper is intended to be published as Hanjing Wu, Milford A. Hanna and David D. Jones. 2012. Feedlot manure-derived biochar effects on nitrogen and phosphorus leaching.

Abstract

Due to increasing world food demand, large amounts of fertilizer are applied to soil to improve crop yields. Excess fertilizer application or poor fertilizer management tends to cause nutrient leaching, polluting the surrounding environment. Applying biochar has been shown to increase soil fertility and reduce nutrient leaching. As a byproduct of gasification or pyrolysis processes, biochar could effectively sequester carbon in soils and, thus, reduce greenhouse gases. Therefore, biochar produced from gasification of animal waste has a two-fold benefit to the environment: (1) its main product, syngas, is a renewable energy source for power generation or chemical production and (2) the biochar provides additional soil management options. For this project, biochar was produced from gasification of feedlot manure in a laboratory-scale fluidized-bed gasifer. Biochar effects on total phosphorus (TP) and ammonium nitrogen (NH_4^+-N) leaching from two contrasting soils (clay and sandy loam soils) were examined during four leaching events within three months. The application rate of biochar to the soil was 0, 1:200, 1:100 and 1:50 w/w, indicated as BC0 (control), BC0.5%, BC1%, and BC2%, respectively. Results showed that biochar addition increased water holding capacity of both soils, and the higher the biochar addition rate was, the less leachate was collected. 5.0% and 6.6% cumulative leaching amount from BC0 was reduced by BC2% for clay and sandy loam soils, respectively. Except the first leaching event, more cumulative TP was leached from soil columns with biochar additions. The most cumulative TP leaching was from BC1%. Conversely, BC1% reduced cumulative NH_4^+-N by 5% and 19% for clay and sandy loam soils, respectively. Therefore, it was concluded that biochar had the potential to retain water and NH_4^+-N. But biochar derived from feedlot manure caused more P in the

leachate during our experiment except for a temporary P reduction during the first leaching event. In summary, biochar utilization, as a soil additive, is still in its infancy, and more experimental data are needed before large scale application of biochar in agriculture can be recommended.

Kew words: biochar, clay soil, sandy loam soil, leaching, total phosphorous, ammonium-nitrogen

1. Introduction

Fertilizer has been used widely in soil to improve plant growth. It is estimated that at least 30% to 50% of crops yield are attributable to commercial fertilizer nutrient inputs.[1] Each year, millions of tons of fertilizer are applied to soils, and the consumptions of N, P and K are close to 30 million tons per year on American farmland.[2]

However, excess fertilizer nutrients can move into surface water, or leach into ground water, if improperly managed.[3] Nutrient leaching contributes to fresh water eutrophication, which is of great concern in terms of the environment. Nitrogen and phosphorus pose the greatest threats to water quality. For instance, 60% to 90% of P moves with eroded soil, and it is a major source of water quality impairment in lakes.[3] Applying slow-release fertilizer and increasing adsorption sites have been considered as two common ways to reduce nutrient leaching.[4]

Biochar is defined as the carbonaceous residue of incomplete burning of carbon-rich biomass.[5] As a byproduct of pyrolysis or gasification composed mainly of carbon, biochar can sequester carbon and therefore, reduce greenhouse gas emissions. It also can be used as the nutrient source directly because of its inherent nutrients including N, P, K, Ca, Mg, S and micronutrients.[6] In addition, biochar has been shown to increase soil fertility by improving water retention, lowering soil acidity and density, along with increasing microbial activity. In particular, it has been found to reduce nutrient leaching by itself, as well as after incorporation within soil.[7]

Research has been conducted on biochar effects on nutrient leaching. Laird et al.[8] quantified the impact of soil-biochar amendments on nutrient leaching following swine manure application for a Midwestern agricultural soil, and they found out that the total amount of P leached from the manure amended columns during weeks 0–45 decreased with increasing levels of biochar, which may due to the bounding of added P to the biochar. In addition, six solid wood and ash/charcoal residues were collected and tested for their nutrient retention qualities by Dünisch et al.[9] They pointed out that ash/charcoal residues adsorbed up to twice as much as N and up to 100 times more K than the treated wood residues. Besides that, they also concluded that binding of N and K to the C-matrix within residues during impregnation was different from P, which was not or only weakly fixed to the C-matrix.Though N, P and K are the nutrients of greatest interest to researchers, other nutrients also have been taken into account in leaching experiments. For instance, Novak et al.[10] tested the impact of pecan shell based biochar additions on soil fertility characteristics and water leachate chemistry for Norfolk loamy sand. Experimental results reflected the high sorption capacity of biochar for Ca, P, Zn, and Mn.

Investigations on the biochar effects on nutrient leaching are limited, and no information is available about the characteristics of biochar from gasification of feedlot cattle manure. The major goal of animal manure gasification is to utilize animal waste for renewable energy, and the study of its byproduct biochar provides additional knowledge to manage animal waste. As Spokas et al.[11] stated, biochar application to the soil is not a one-size fits all paradigm, but instead a case-by-case study, owing to its both negative environmental and positive agronomic effects. Consequently, the feedlot manure derived biochar effects on fertilizer leaching from two contrasting soils (clay and sandy loam) were examined. The leaching of ammonium nitrogen (NH_4^+-N) and total P (TP) from the biochar amended soil columns were recorded and analyzed during four leaching events in three months. NH_4^+-N is the inorganic form of nitrogen fertilizer, and its loss into surface water contributes to the poisoning of aquatic organisms if its concentration is larger than 2.5 mg L^{-1}.[12] TP includes the inorganic and organic forms of P, and its runoff is the main cause of eutrophication.

2. Materials and Methods

2.1 Biochar

The gasification experiment was conducted using a laboratory-scale fluidized-bed gasifier. Detailed information of the gasifier set-up and operation were presented by Kumar et al.[13] and Wu et al.[14]

Feedlot cattle manure collected from the University of Nebraska Agricultural Research and Development Center was used as the raw material. Before gasification, the cattle manure samples were air dried, ground, and sieved to particle size less than 2.5 mm. The temperature of the gasifier was set at 650^{o}C, and the equivalence ratio was 1.0. Biochar was collected at the bottom of a cyclone separator. Ultimate analyses of the biochar samples were conducted by Twin Ports Testing, Inc. (Superior, WI, USA).

2.2 Soil

Two different soils (clay and sandy loam soils) prevalent in Nebraska were used for the leaching experiments. Soils were air dried, and then ground to obtain < 2 mm fraction.

2.3 Equipment

The leaching experiment was conducted in specially designed PVC columns (25 cm high and 10 cm internal diameter) with a leachate collection outlet and an airtight screw-on cap. The soil and biochar mixtures column used in this project is shown in Figure 1.

2.4 Experimental Design

Biochar was added slowly to the 1 kg soil to bring the final biochar content to 0, 5, 10, 20 g kg^{-1} of the dry soil, indicated as BC0 (control), BC0.5%, BC1% and BC2%, respectively. The packing density of the soil was 1.1 g cm^{-3}. There were two replications for each experimental treatment.

2.5 Methods

At the beginning of the leaching experiment, the soil-biochar mixtures were packed into the columns. A small cotton ball was placed between the leachate outlet and the column to stop the soil moving into the leachate. Then 400 ml of distilled water were poured onto the soil and biochar mixtures, making the water filled pore space (WFPS) equal to 0.85. The first leaching event took place one day after packing and wetting. A leaching event consisted of adding 300 ml nutrient solution to each column. Nutrient solution contained N (applied at 90 kg N ha^{-1} as NH_4NO_3) and P (applied at 30 kg P ha^{-1} as KH_2PO_4). After 24 h, the leachate was collected from the outlet in a 500 ml polyethylene bottle. Leachate samples were analyzed for NH_4^+-N and TP. NH_4^+-N concentrations were tested by the Water Science Laboratory, University of Nebraska-Lincoln. An ascorbic acid method was applied to test the TP concentration by a UV spectrophotometer (Model: UV-1800, Shimadzu Co., Kyoto, Japan).

The second leaching event took place one month later at which time 300 ml nutrient solution with N (applied at 45 kg N ha^{-1} as NH_4NO_3) and P (applied at 30 kg P ha^{-1} as KH_2PO_4) were added to each column and the leachates were collected and analyzed for N and P levels. For the third and fourth leaching events, the same procedure was repeated two months and three months later. All the columns were held in the laboratory at room temperature for the duration of the research, with a lid to avoid water evaporation between leaching events.

2.6 Statistical Analyses

One-way analyses of variance (ANOVA) were used to analyze the nutrient leaching data by SAS 9.2 (SAS Institute Inc., Cary, NC, USA). Least square means of each treatment were compared and *P*-value <0.05 was considered as significantly different.

3. Results and Discussions

3.1 Characteristics of Biochar

The ultimate analysis results of biochar are shown in Table 1. The relatively high content of ash in the biochar resulted from high ash content of the feedlot manure, which was collected from the soil surface of the feedlot. Similarly, ash contents of chicken litter biochars have been reported to be up to 45%.[15,16]

For the volatile matter of the biochar, carbon (C) composed the highest content, which was more than 25%. C content is of primary interest when considering long-term carbon sequestration in soils.[17] This is due to the fact that C in biochar is extremely recalcitrant, with a residence time 10 to 10,000 times longer than that of most soil organic matter.[16] Gryze et al.[18] also emphasized that the thermochemical conversion of organic matter to biochar greatly increases the recalcitrance of C, making it more resistant to biological, physical and chemical decomposition. Biochar C content is determined by the feedstock and conversion conditions. Its concentration within biochar increased with temperature.[17] Recently, due to the growing global warming concerns, considerable attention has been given to biochar as a potential tool to relieve greenhouse gas effect by sequestering C. For example, Woolf et al.[19] estimated that current net emissions of greenhouse gases could be reduced by 12% if biochar was incorporated into soil.

In addition, compositions of other biochars, as reported in the literature,[20] are shown in Table 2. When compared with biochar produced from gasification of feedlot manure in current research, it was found that characteristics of biochar varied depending on the raw material and the gasifying temperature. It is accepted that temperature influences biochar functionally and that biochar produced at a higher temperature is more aromatic and has higher alkalinity.[21] Gaskin et al.[22] also noted that surface area and ash content increased, but surface functional groups decreased as thermochemical conversion temperature increased.

3.2 Water Retention

Although the same amount of nutrient solution was applied to each column during each leaching event, the amount of leachate varied. Detailed information of the cumulative leaching amounts is shown in Figure 2. It can be observed that biochar amended columns held more water than soil columns without biochar, for both soils. Also, a higher biochar addition rate led to a lower amount of leachate collected. Specifically, BC1% and BC2%

significantly reduced the leaching amount for clay soil, while BC0.5%, BC1% and BC2% all significantly reduced the leaching amount for the sandy loam soil. 5.0% and 6.6% cumulative leaching amounts from the control were reduced by BC2% for both clay and sandy loam soils. Much more leachate was collected from sandy loam soil columns, which was about twice as much as the water leached from the clay soil columns. This was due to the relatively poor water holding capacity of sandy loam soil compared to clay soil. The impact of biochar on water retention of the soil may have resulted from specific characteristics of biochar, such as highly porous and large specific surface area.[23] Another possible explanation is the improved aggregation or structure of the soil by biochar addition.[16] While it is generally believed that biochar has the potential to increase water retention, Day et al.[24] found that some biochar produced at relatively lower temperature was hydrophobic, which may limit its water holding capacity.

3.3 TP Leaching

The TP leaching amounts for the four leaching events and their cumulative leaching amount are shown in Figure 3 and Figure 4, respectively. During the first leaching event, the TP leached from the control column was lower than that from BC0.5%, BC1% and BC2% for both clay and sandy loam soils. However, during the second, third and fourth leaching events, more TP was leached from biochar amended columns as shown in Figure 3. From the cumulative leaching point of view, the least amount of TP leached was from the BC0, and the most was from BC1% for both clay and sandy loam soils. In particular, both BC1% and BC2% significantly increased TP leaching for clay soil, while for sandy loam soil, all biochar amended columns (BC0.5%, BC1% and BC2%) significantly increased TP leaching. Results indicated that biochar addition increased TP leaching in the experimental period, except less TP was leached during the first leaching event. On the other hand, higher biochar addition did not cause more TP leaching. Less TP was leached from BC2% than BC1% for two soils. Therefore, it can be seen that biochar can adsorb P temporarily within a short time (24 h), which may have been due to the highly porous structure and large surface area of biochar or the anion exchange capacity of biochar. However, after that, in the following three months, more P was leached from biochar amended columns, which may because of the weak chemical bound of P to the biochar indicated by Dünisch et al.[9] Several other mechanisms may also lead to that result.

Firstly, nutrient solution was added onto soil columns every month which may have led to over fertilization for nominal agronomic needs. As a result, P may desorb from biochar and move into the leachate after the start-up period. Secondly, biochar itself also contains P, which may cause more P leaching afterwards. As pointed out by Sika (2012),[25] the total P content was typically higher in biochars produced from feedstocks of animal origin than those of plant origin. Thirdly, biochar is considered a promoter of microbial activity and P mineralization,[7] and P in organic form from the soil may be released during the mineralization process resulting in more available P for plant uptake. Furthermore, this is not a plot experiment and no plants were grown to adsorb the available P. Overall, it is generally accepted that biochar can alter P availability, but the mechanism is not well

3.4 Ammonium Nitrogen Leaching

NH_4^+-N leaching amount during the four leaching events, and its cumulative leaching amounts, are shown in Figure 5 and Figure 6, respectively. Month to month, different leaching patterns were observed. The least cumulative NH_4^+-N leaching amount was from BC1%, and the most was from BC2% for both soils. 5% and 19% cumulative leaching amounts from the control were reduced by BC1% for clay and sandy loam soils, respectively. A similar result was reported by Ding et al.,[26] who pointed out that the application of 0.5% bamboo biochar to the multi-layered soil columns reduced cumulative losses of NH_4^+-N at 20 cm by 15.2% in 70 days.

From the statistical analysis, for clay soil, BC2% significantly increased NH_4^+-N leaching, while there was not much difference among BC0, BC0.5% and BC1%. In addition, for sandy loam soil, BC2% significantly increased NH_4^+-N leaching, while BC1% significantly reduced the cumulative leaching. Much more NH_4^+-N was leached from sandy loam soil columns than the clay soil columns as with TP leaching.

Consequently, we concluded that the addition of 1% biochar can reduce NH_4^+-N leaching to some extent, especially with sandy loam soil, but higher biochar addition would have adverse effects. Like the study by Xing et al.[27] with eucalyptus chips biochar effects on NH_4^+-N leaching, it was concluded that the addition of 1% biochar reduced the N leaching, while excessive biochar increased the leaching. Similarly, Hyland et al.[28] documented a 7% biochar (from poultry manure mixed with sawdust) addition increased NH_4^+-N leaching.

The adsorption of NH_4^+-N by biochar may have been due to its cation exchange capacity (CEC).[26] CEC of biochar is dependent on temperature, feedstock and storage time. Proposed by Gaskin et al.,[22] CEC of biochar produced at 500 ^oC was significantly less than that produced at 400 ^oC. Moreover, aged biochar tended to have a high CEC.[16]

On the other hand, the reason for the increasing NH_4^+-N leaching by BC2% is much more complicated, and several mechanisms may contribute to it. Firstly, some NH_4^+-N may be leached from biochar. That's because small amounts of NH_4^+-N in leachate were determined to be from biochars derived from poultry litter, peanut hulls and pine chips, respectively.[22] Secondly, as Spokas et al.[11] indicated, biochar was found to react with various nitrogen components and hence, influence soil nitrogen cycle and may cause more N leaching. It is crucial to mention that some biochars may be capable of adsorbing NO_3^- versus NH_4^+-N (positively versus negatively charged biochars).[21]

4. Summary

In this project, biochar effects on TP and NH_4^+-N leaching were examined and analyzed. Biochar was produced from gasification of feedlot cattle manure in an experimental-scale gasifier. Four leaching events within three months were applied to clay and sandy loam soil columns. For each soil, there were four experimental treatments: BC0 (control), BC0.5%, BC1% and BC2%. Our conclusions are as follows:

First, biochar derived from cattle manure contained high ash content, due to the high ash content of manure samples. The relatively high level of C provides a mechanism for biochar to reduce greenhouse gases. Composition of biochar varied according to both feedstock and thermochemical conversion conditions.

Secondly, biochar addition increased the water holding capacity of both soils. The higher the biochar addition rate was, the more water was retained during our experimental period. The 5.0% and 6.6% cumulative leaching amounts from the control were reduced by BC2% for clay and sandy loam soils, respectively.

Thirdly, BC1% and BC2% increased TP cumulative leaching significantly for both clay and sandy loam soils. The highest cumulative TP leaching was from BC1%. The mechanism is not fully understood, but P desorption after the first leaching event and P mineralization process are possible explanations.

Fourthly, similar NH_4^+-N leaching trends were observed from both soils. For example, the most cumulative NH_4^+-N leaching was from BC2%, and the least was from BC1%. In addition, BC1% reduced NH_4^+-N cumulative leaching from the control by 5% and 19% for clay and sandy loam soils, respectively. CEC of biochar could be the dominant reason to retain NH_4^+-N.

In summary, biochar addition to the soils influenced both NH_4^+-N and P leaching for both soils, but the effects were somehow adverse. Much more experimental work on biochar characteristics and its impacts on nutrients are needed before larger application of biochar in agriculture can be recommended.

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Table 1. Ultimate analysis of biochar from gasification of feedlot manure

Element	Composition (w.t. %)
Carbon (C)	25.51
Hydrogen (H)	1.78
Nitrogen (N)	1.75
Oxygen (O)	6.67
Sulfur (S)	0.30
Ash	59.20
Moisture	4.80

Table 2. Biochar compositions (dry basis) from different feedstock and thermochemical conditions[20]

Feedstock	Pyrolysis condition	C	H	O	N	S	Ash
Poultry litter	Pyrolysis at 350 ^oC	46.10	3.70	8.60	4.90	0.78	35.90
Poultry litter	Pyrolysis at 700 ^oC	44.00	0.30	<0.01	2.80	1.00	52.40
Switchgrass	pyrolysis at 250 ^oC	55.30	6.00	35.60	0.43	0.05	2.60
Switchgrass	pyrolysis at 500 ^oC	84.40	2.40	4.30	1.07	0.06	7.80

Figure 1. The soil and biochar mixtures column

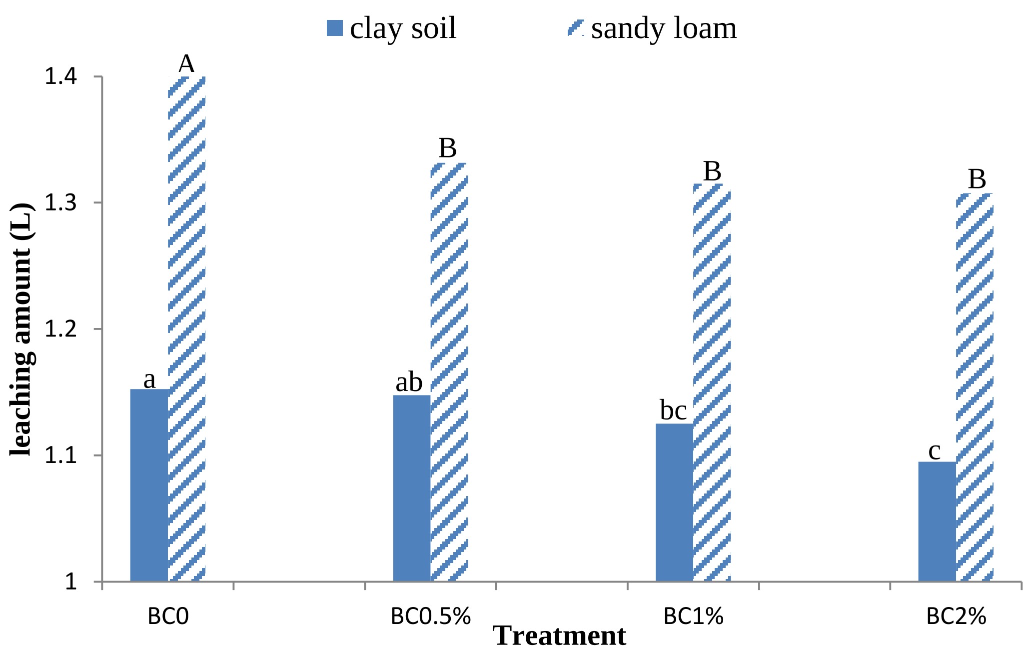

Figure 2. Cumulative leaching amounts for clay and sandy loam soils

(Different lowercase letters and uppercase letters above the bars indicate statistically significantly different (*P*<0.05) among treatments for clay soil and sandy loam, respectively.)

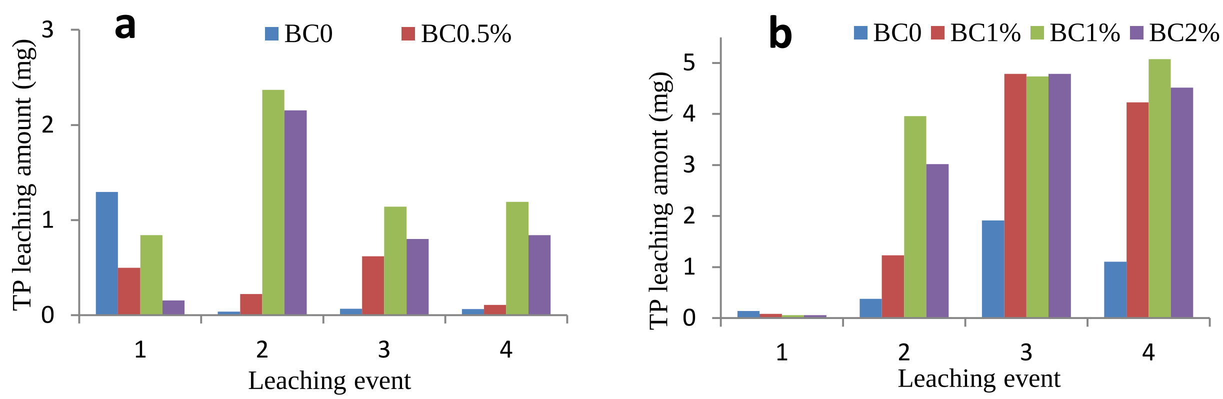

Figure 3. TP leaching amounts during four leaching events for clay soil (3a) and sandy loam (3b)

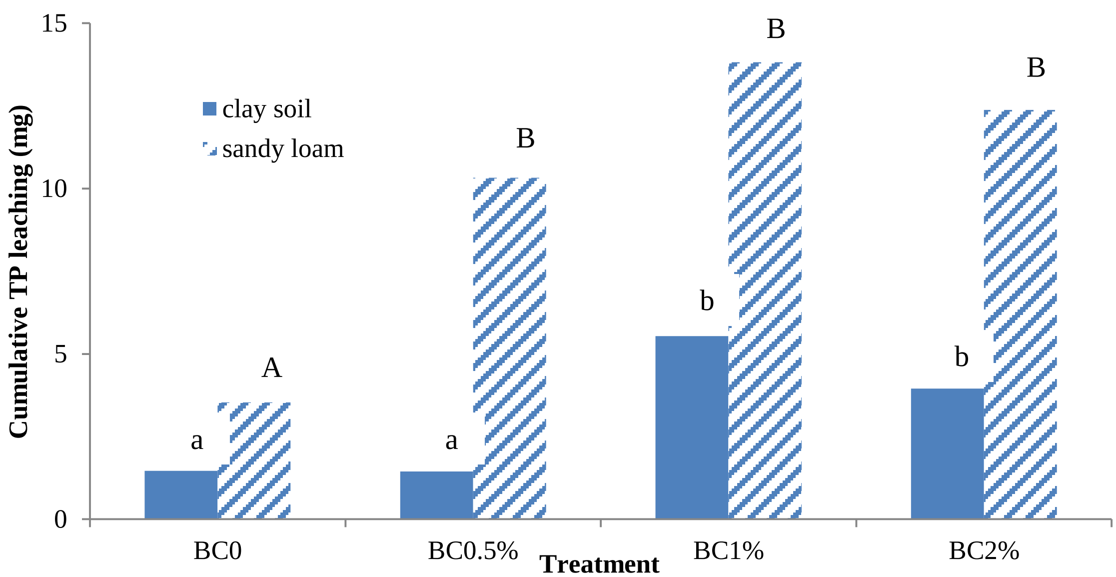

Figure 4. Cumulative TP leaching amounts for clay and sandy loam soils

(Different lowercase letters and uppercase letters above the bars indicate statistically significantly different (P<0.05) among treatments for clay and sandy loam soils, respectively.)

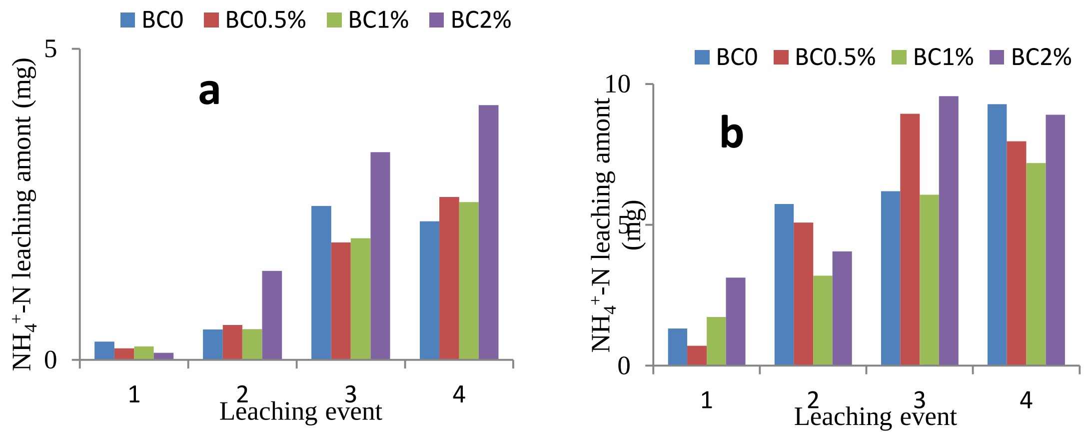

Figure 5. NH_4^+-N leaching amounts for clay soil (5a) and sandy loam soil (5b) during four leaching events

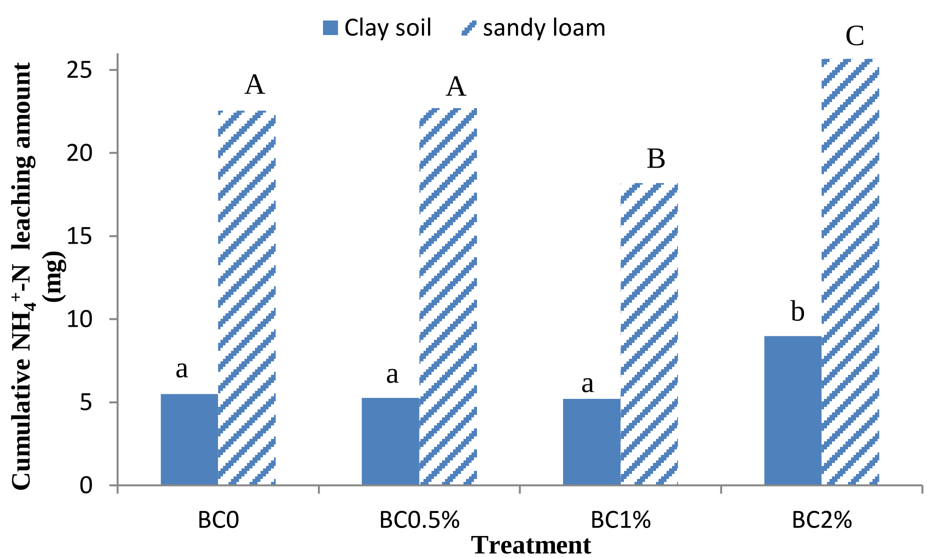

Figure 6. Cumulative NH_4^+-N leaching amounts for clay soil and sandy loam soil

(Different lowercase letters and uppercase letters above the bars indicate statistically significantly different (P<0.05) among treatments for clay and sandy loam soils, respectively.)

CHAPTER VI

LIFE CYCLE ASSESSMENT OF GREENHOUSE GAS EMISSIONS OF FEEDLOT MANURE MANAGEMENT PRACTICES: LAND APPLICATION VERSUS GASIFICATION

This research paper is intended to be published as Hanjing Wu, Milford A. Hanna and David D. Jones. 2012. Life cycle assessment of greenhouse gas emissions of feedlot manure management practices: land application versus gasification.

Abstract

Animal waste is an important source of anthropogenic GHG emissions, and in most cases, manure is managed by land application. Nevertheless, due to the huge amounts of manure produced annually, alternative manure management practices have been proposed, one of which is gasification, aimed to convert manure into clean energy-syngas. Syngas can be utilized to provide energy or power. At the same time, the byproduct of gasification, biochar, can be transported back to fields as a soil amendment. Environmental impacts are crucial in selecting the appropriate manure strategy. Therefore, GHG emissions during manure management systems (land application and gasification) were evaluated and compared by life cycle assessment (LCA) in our study. LCA is a universally accepted tool to determine GHG emissions associated with every stage of a system. Results showed that the net GHG emissions in land application scenario and gasification scenario were 119 and -643 kg CO_2-eq for one tonne of dry feedlot manure, respectively. Moreover, sensitive factors in the gasification scenario were efficiency of the biomass integrated gasification combined cycle (BIGCC) system and energy source of avoided electricity generation. Overall, due to the environmental effects of syngas and biochar, gasification of feedlot manure is a much more promising technique as a way to reduce GHG emissions than is land application.

Key words: feedlot manure, land application, gasification, greenhouse gas emissions, life cycle assessment

1. Introduction

Greenhouse gases (GHGs) effectively absorb thermal infrared radiation, emitted by the Earth’s surface, the atmosphere itself, and clouds. The heat trapping process within the surface-troposphere system by GHGs is called the greenhouse gas effect [1]. Naturally occurring GHGs include water vapor, CO_2, methane (CH_4), nitrous oxide (N_2O), and ozone (O_3) [1,2]. The increase in GHG concentration has been accepted widely as the major cause of current global warming, and animal manure is an important source of GHG [3]. In 2010, CH_4 emissions from manure management represented about 8% of total CH_4 emissions from anthropogenic activities, and manure management also was a small source of N_2O emissions [2].

Land application is the most common way to use animal manure, with the purpose of using manure nutrient as the fertilizer. Around 83% of feedlot manure typically is processed by land application [4]. However, applying feedlot manure to the surrounding cropland may become unsustainable for large feedlots, as it can exceed the carrying capacity of local ecosystems leading to environmental and health concerns [5]. Gasification is an alternative way to manage animal waste. The principle of gasification is to decompose organic matter into useful energy such as syngas. In order to generate electricity and heat, syngas produced from gasification could be utilized in energy conversion devices, such as boilers and gas turbines. For small-scale power plants, typically syngas is combusted in a stationary IC engine with a generator and provisions for heat recovery. For larger scale operations, integrated gasification/combined cycle (IGCC) technology can be applied to generate electricity and heat [6]. Further, biochar, as the byproduct of gasification, has attracted growing interest globally as a soil amendment [7]. However, the nutrient value of biochar differs considerably due to the variation among the feedstock characteristics and gasifier operating conditions [8].

GHG emissions are a major factor when selecting the appropriate animal waste management practice and life cycle assessment (LCA) is a universally accepted tool to determine GHG emissions due to its "cradle-to-grave" approach [9]. LCA has been adopted to analyze emissions of GHG for different animal waste management systems. For example, Morrie et al. [10] conducted a LCA for anaerobic digesters on small dairy farms. Also, environmental effects of composting dairy manure were evaluated by Hishinuma et al. [11] by means of LCA. Nevertheless, not much information can be found related to feedlot manure management in terms of GHG emissions. Therefore, the aim of this research was to estimate GHG emissions of feedlot manure management systems (land application and gasification) by LCA. In the land application scenario, feedlot manure was collected, stored and applied as fertilizer onto the field. In the gasification scenario, feedlot manure was gasified to produce syngas and biochar, which were used as the power source and soil amendment, respectively.

2. Methodology

2.1 Goal and Scope

The goal of this study was to evaluate GHG emissions of two feedlot manure management strategies: land application and gasification. The function unit was one tonne of dry feedlot manure. Emission of each GHG was converted into carbon dioxide equivalent (CO_2-eq), which was calculated by multiplying their respective global warming potential (GWP) by the specific mass of each GHG. The GWPs of CH_4, and

N_2O are 25 and 298 times that of CO_2 on a mass basis, respectively, bases on a 100 year horizon [12].

2.2 System Boundaries

System boundaries of the two manure management practices are shown in Figure 1 and Figure 2, respectively. In land application scenario, feedlot manure was collected twice a year (winter and spring), stockpiled and land applied in the fall. The avoided process was the commercial fertilizer utilization due to the manure application. In the gasification scenario, feedlot manure was collected every two months (six times a year). The collected manure was transported to an industrial-scale gasification plant. The technology of biomass integrated gasification combine cycle (BIGCC) was used to generate electricity. Biochar produced from gasification plant was transported back to the field as a soil amendment. Avoided processes were electricity generation from fossil fuel power plant, and fertilizer utilization due to biochar application.

2.3 Data Inventory and Major Assumptions

To make the industrial-scale gasification plant possible (the feeding rate was 1 tonne of dry manure per hour), assuming the feedlot manure was provided by 10 feedlots, each with 500 animal-units (AU). AU was defined as a1000 lb cow or its equivalent [4]. The inventory data were based on the literature references and GREET Model 2012 (Argonne National Laboratory, USA) [13]. Note that emissions from the manufacture of the transportation tools were out of the consideration in this study. In addition, the bioenic CO_2 emissions were not taken into account, because carbon from biomass is part of the natural carbon cycle. The sections below include detailed information of data sources and assumptions for each life cycle stage.

2.4 Feedlot Manure Characteristics

Characteristics of feedlot manure vary widely due to factors of climate, diet, feedlot surface and cleaning frequency [4]. The excreted manure is usually high in moisture content and low in ash content. On the other hand, for collected feedlot manure, water concentration drops because of evaporation, and the fixed solid increases due to its incorporation into the soil. Table 1 shows the characteristics of feedlot manure used in this study, assuming the same characteristics of collected feedlot manure for the two scenarios.

2.5 Manure Collection, Transportation and Land application

In land application scenario, a tractor-mounted front-end loader was used to collect and pile feedlot manure, then the manure was stockpiled, and finally a spreader was used for manure spreading. Heavy-duty trucks were responsible for transportation. The average distance was assumed 5 km from the manure collection site to the storage site, and from the storage site to the designated field [5].

In the gasification scenario, the feedlot manure was collected every two months. The average distance was assumed to be 15 km from the feedlots to the gasification plant [15]. Note that there was no backhaul of trucks, which was used to transport biochar back to the designated field. Based on a feedlot (250 cattle) manure handling system presented by Ghafoori et al. [5], working hours and distance of equipment for one feedlot (500 AU) were adjusted and listed in Table 2. From Table 1, feedlot manure production was 7.9 kg day^{-1}for one AU, the number of heavy-duty trucks (payload=18,144 kg) also were listed in Table 2. It was assumed that diesel was consumed for the front-end loader, heavy-duty trucks and spreaders, and GHG emissions of those equipment were calculated by GREET Footprint Calculator 2012 (Argonne National Laboratory, USA) [16].

2.6 Manure Emissions

GHG emissions from collection, storage and treatment depend on the amount of manure produced, C and N contents, temperature and management method. In general, liquid systems generate relatively more CH_4, while solid systems produce more N_2O [17]. CH_4 and N_2O emissions from annual manure production were estimated by equation (1) and (2), respectively [4]:

$$\text{Methane emissions (kg year}^{-1}\text{)} = VS_{excreted} \times B \times 0.67\ \text{kg m}^{-3} \times MCF \quad (1)$$

where $VS_{excreted}$=Volatile solids excreted (kg year^{-1}),

B=Maximum CH_4 producing capacity on VS (m^3 kg^{-1}),

MCF=CH_4 conversion factor bases on the waste minimization system (%), and

0.67=CH_4 density at stp (293K, 101.3 kPa).

N_2O emissions are estimated by equation (2):

$$N_2O\ \text{emissions (kg year}^{-1}\text{)}=1.57 \times M_N \times MF_{N2O} \qquad (2)$$

where M_N=N excretion rate, kg year^{-1}, and

MF_{N2O}=Nitrous oxide factor.

$VS_{excreted}$ and N excretion rates are shown in Table 1. The estimated values of B, MCF and MF_{N2O} were 0.33, 1.5% and 0.02 [4], respectively.

In the land application scenario, emissions from the feedlot manure occurred in every step, from collection, to storage, to land application. On the other hand, in the gasification scenario, once the feedlot manure was collected every two months for gasification, emissions were prohibited in the gasifier. In this study, manure emissions were based upon manure production from 10 feedlots during one year. Thus, it was assumed that manure emissions from the gasification scenario were 1/6 of the emissions from the land application scenario based on the manure exposure time (2 months to 12 months) during one year cycle.

2.7 Avoided Fertilizer Utilization

In land application scenario, the N, P and K contents of feedlot manure reduced the amount of commercial fertilizer applied to the agriculture system; therefore, GHG emissions related to fertilizer application were avoided. The initial nutrient content of feedlot manure is shown in Table 1. It was assumed that 24% of N was lost to the environment due to volatilization of NH_3 and N_2O [18], while no P and K was lost. The emission factors used for each type fertilizer (N, P, or K) was based on the avoided life cycle emissions from fertilizer production. We assumed emission factors of one kilogram N, P, and K were 8.9, 1.8 and 0.96 kg CO_2-eq, respectively [19].

2.8 Gasification Plant

In the gasification scenario, biomass integrated gasification combined cycle (BIGCC) technology was applied to process the collected manure. The schematic diagram of the BIGCC system is shown in Figure 3 [20-23]. The basic components included a biomass dryer, a gasifier, a gas cleanup system, a gas turbine, a heat recovery steam generator (HRSG) and a steam turbine. Major assumptions of the BIGCC system are listed in Table

3. Feedlot manure was dried, ground and then fed into the gasifier to generate syngas. A cyclone separator was used to separate the biochar from the syngas. Tar and particles were removed by a gas cleaning system. A gas turbine was used to generate electricity by combustion of the syngas. Part of the hot exhaust gas from the gas turbine was used to dry the feedlot manure and the remaining hot exhaust gas was introduced into HRSG and steam turbine for additional electricity.

Although there were no direct data presented on GHG emissions of gasification system of feedlot manure processing, the reference data of the GHG emissions during thermochemical conversion of wood chips within different thermochemical conversion processes are shown in Table 4. GHGs emissions included plant construction and operation, without direct CH_4 and N_2O outputs from the gasification of wood chips. It can be seen that GHG emissions varied from 3 to 9 g CO_2-eq per MJ energy produced. Thus, GHG emissions were assumed to be 6 g CO_2-eq per MJ energy of BIGCC system in this study.

2.9 Avoided Electricity Generation

Since electricity was generated from the feedlot manure through the BIGCC technology, electricity generation from fossil fuels was avoided. However, GHG emissions vary among different energy sources. Table 5 presents GHG emissions of electricity generation from three types of fossil fuels: petroleum, nature gas and coal (GREET Model 2012) [13]. In this analysis, avoided electricity generation was assumed from petroleum.

2.10 GHG Emissions Reduction from Biochar Application

Biochar composition and yield depend highly on the thermochemical conversion operation and feedstock characteristics. Typically, the order of the biochar yield is slow pyrolysis>fast pyrolysis>gasification [26]. In this study, biochar yield was assumed to be 20% of the dry matter. Biochar effects on GHG emissions reduction can be divided into four aspects: 1) carbon sequestration; 2) N_2O emission reduction when applying biochar in the soil; 3) displacing commercial fertilizer, and 4) enhancement of agronomic efficiency [27]. We assumed that 26% of the biochar was carbon, based on the ultimate analysis of the biochar derived from feedlot manure gasification [28], and 75% of the carbon in biochar was sequestered in the soil [29]. Biochar was transported back by heavy-duty trucks and a spreader was used to apply the biochar in the field. GHG emissions of heavy-duty trucks and the spreader were discussed in previous section. The degree of biochar effects on agronomy depends on a number of factors, including soil properties, geographical attributes, biochar composition, and interactions between these unknown factors [30]. The application rate was assumed to be 5 tonnes per hectare, and ranges of GHG emissions reduction for one hect are of five different crops are shown in Table 6 [27]. The average value ranges from -0.25 to -1.22 tonne CO_2-eq, and the average medium value of -0.71 tonne CO_2-eq was adopted.

3. Results and Discussions

3.1 Net GHG Emissions of Land Application Scenario

Detailed GHG emissions from each life cycle stage of land application scenario are show in Table 7. Avoided GHG emissions were derived only from displacing fertilizer utilization, which was 177 kg CO_2-eq per tonne dry feedlot manure. Manure emissions accounted for most of the GHG emissions, which was 98.8 %. The net GHG emission was 119 kg CO_2-eq for one tonne of dry feedlot manure.

3.2 Net GHG Emissions of Gasification Scenario

GHG emissions from each life cycle stage of gasification scenario are shown in Table 8. Manure emissions and gasification plant operation, accounted for 63.7 % and 31.8 % of the total GHG emissions. In addition, avoided electricity generation and carbon sequestration were 76.1 % and 20.0 % of the total GHG emissions reduction, respectively. The net GHG emissions for one tonne of dry feedlot manure in the gasification scenario were -643 kg CO_2-eq.

3.3 Sensitivity Analysis

When building the life cycle inventory, some important assumptions were made. In order to assess the robustness of the result and impacts of parameters on the outcome, a sensitivity analysis was conducted. Results of the sensitivity analysis are presented in Table 9.

One major uncertain assumption in land application scenario was the avoided GHG emissions of fertilizer utilization. Typically, GHG emissions fall in the range of 4.75–13.0 kg CO_2-eq, 0.52–3.09 kg CO_2-eq and 0.38–1.53 kg CO_2-eq for 1 kg of N, P and K fertilizer, respectively [31]. If the highest and lowest fertilizer emission factors were assumed, net GHG emissions decreased and increased by 75%, respectively. That means the results in the land application case are very sensitive to the assumption related to the emission factor of the fertilizer utilization.

Moreover, four uncertain assumptions were made in the gasification scenario. The first uncertainty was the gasification plant emissions. GHG emissions of gasification plant were assumed to be between 3 and 9 g CO_2-eq per MJ energy, resulting in the decrease and increase in the net GHG emissions of 1.82% respectively. Therefore, it can be seen that net GHG emissions in the gasification scenario is not sensitive to gasification plant emissions. The second uncertainty was the BIGCC efficiency, which varied by the system design and operation. Assuming the efficiency was 35% and 45%, the changes in net GHG emissions increased and decreased by 18.7%, respectively. Thus, the BIGCC efficiency is a major factor influencing the final outcome. The third uncertainty was the energy resource of avoided electricity generation. If the avoided electricity was produced by nature gas and coal, other than petroleum, the net GHG emissions increased by 41.4% and decreased by 9.9%, respectively. The fourth uncertainty was the biochar effects on agronomy. Biochar effects on GHG emissions reduction assumed 0.25 and 1.22 tonnes CO_2-eq per hector, resulting in the final net GHG emissions increased by 2.86% and decreased by 3.17%, respectively. Overall, it can be concluded that the outcome in the gasification scenario is sensitive to factors of BIGCC efficiency and energy sources of avoided electricity generation.

4. Conclusions

In this study, GHG emissions of two feedlot manure management practices (land application and gasification) were estimated by LCA. In addition, a sensitivity analysis was conducted to test impacts of important variables. The net GHG emissions were 119 and -643 kg CO_2-eq per tonne dry feedlot manure for land application scenario and gasification scenario, respectively. From the sensitivity analysis, the replaced fertilizer emissions changed the net GHG emissions up to 75% in the land application scenario. In the gasification scenario, sensitive factors were energy source of avoided electricity and BIGCC efficiency. On the other hand, gasification plant emissions and biochar effects on agronomy did not influence the result much. Our analysis shows that in the gasification scenario, manure emissions were reduced by the gasification process, and at the same time, syngas and biochar, which can be further used as the power source and soil amendment, played an important role in GHG emissions reduction. Consequently, the gasification scenario provides an alternative solution to reduction in GHG emissions.

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Table 1. Characteristics of feedlot manure per animal unit

Component	Excreted	Collected	Unit	References
Weight	51.2	7.9	kg d^{-1}	[4]
Moisture	884	450	g kg^{-1}	[4]
TS	5.91	4.4	kg d^{-1}	[4]
VS	5.44	2.2	kg d^{-1}	[4]
FS	0.47	2.2	kg d^{-1}	[4]
N	0.30	0.095	kg d^{-1}	[4]
P	0.094	0.064	kg d^{-1}	[4]
K	0.21	0.014	kg d^{-1}	[4]
C:N ratio	10	13	-	[4]
Higher heating value (DAF)	-	15,000	kJ kg^{-1}	[14]

(Note: TS, VS and FS are total solids, volatile solids and fixed solids, respectively)

Table 2. Manure handling equipment description of two scenarios for one feedlot (500 AU)

Equipment	Working time/distance for land application scenario	Working time/distance for gasification scenario	Description
Front-end Loader	9 hours	3 hours	Piling up manure and loading to trucks
Heavy-duty trucks	5 km	15 km	80 trucks and 84 trucks needed for land application scenario and gasification scenario, respectively per year
Spreader	30 min per load	30 min per load	Application of feedlot manure and biochar for land application scenario and gasification scenario, respectively

Table 3. Major assumptions of BIGCC system

BIGCC system	Value	Reference
Capacity factor	0.9	-
Dry matter feeding rate	1 t h^{-1}	-
Moisture mass fraction of feeding manure	15%	-
Efficiency of the dryer	95%	[23]
Latent heat for water evaporating	2.5 MJ kg^{-1}	[23]
Gas turbine power efficiency	28.7%	[24]
Steam turbine power efficiency	15.1%	[24]
Auxiliary power need	3.8%	[24]

Table 4. GHG emissions for different gasification systems of wood chip [25]

Gasification systems	CO_2 (g MJ^{-1})	CH_4 (g MJ^{-1})	N_2O (g MJ^{-1})	GHG (g MJ^{-1})
Combined heat and power (small scale) by gasification of wood chip from short rotation coppice (option A)	5±1	0.001	-	5±1
Combined heat and power (small scale) by gasification of wood chip from short rotation coppice (option B)	4±1	-	-	4±1
Electricity by gasification of wood chips from forestry residues (large scale)	7	0.003	-	7
Electricity by gasification of wood chips from short rotation coppice (option A)	8±1	0.003	0.001	8±1
Electricity by gasification of wood chips from short rotation coppice (option B)	7±1	0.003	-	7±1

(Note: option A and option B are two different gasification operations from the reference.)

Table 5. GHG emissions of electricity generation from three types of fossil fuels [13]

	Petroleum	Nature gas	Coal
CH_4 (g MJ^{-1})	0.003	0.0008	0.003
N_2O (g MJ^{-1})	0.001	0.003	0.003
CO_2 (g MJ^{-1})	245.8	125.0	274.2

Table 6. GHG emissions for one hectare when the application rate is 5 tonnes per hectare [27]

Crop	Low (tonne CO_2-eq)	Medium (tonne CO_2-eq)	High (tonne CO_2-eq)
Canola	-0.05	-0.22	-0.39
Broccoli	-0.66	-1.56	-2.57
Wheat (UK)	-0.28	-0.87	-1.49
Maize	-0.19	-0.67	-1.19
Wheat (Australia)	-0.06	-0.25	-0.45
Average	-0.25	-0.71	-1.22

(Note: Negative value indicates GHG emissions reduction)

Table 7. GHG emissions for every life cycle stage in land application scenario

Life cycle stage	kg CO_2-eq per tonne dry feedlot manure	%
Manure collection	0.992	0.336
Transportation	0.640	0.217
Spreading	1.90	0.642
Manure emissions	292	98.8
Displacing fertilizer utilization	-177	100
Net emissions	119	-

(Note: Negative value indicates GHG emissions reduction)

Table 8. GHG emissions for every life cycle stage in gasification scenario

Life cycle stage	Value (kg CO_2-eq per tonne dry manure)	%
Manure Collection	0.992	1.35
Manure Transportation	1.02	1.38
Manure emissions	46.9	63.7
Gasification plant emissions	23.4	31.8
Biochar transportation	1.03	1.40
Biochar spreading	0.216	0.293
Avoided electricity generation	-545	76.1
Carbon sequestration	-143	20.0
Biochar effects on agronomy	-28.4	3.96
Net emissions	-643	-

(Note: Negative value indicates GHG emissions reduction)

Table 9. Sensitivity analysis of major assumptions of two scenarios

Assumptions	Used in this study	Alternative assumptions	GHG emissions change	Alternative assumptions	GHG emissions change
Land application scenario					
Fertilizer emission factor(kg kg^{-1})	8.9,1.8 and 0.96 for N, P and K, respectively	13, 3.09 and 1.53 for N, P and K, respectively	-75%	4.75, 0.52 and 0.38 for N, P and K, respectively	75%
Gasification scenario					
Gasification plant emissions (g MJ^{-1})	6	3	-1.82%	9	1.82%
BIGCC efficiency	40%	35%	18.7%	45%	-18.7%
Avoided electricity generation	Oil-fired power plant	Nature gas fired power plant	41.4%	Coal-fired fired power plant	-9.9%
GHG emissions from biochar (tonne ha^{-1})	-0.71	-0.25	2.86%	-1.22	-3.17%

(Note: Percentage increase indicates an increase in the overall emissions, even where the net GHG emissions remain negative.)

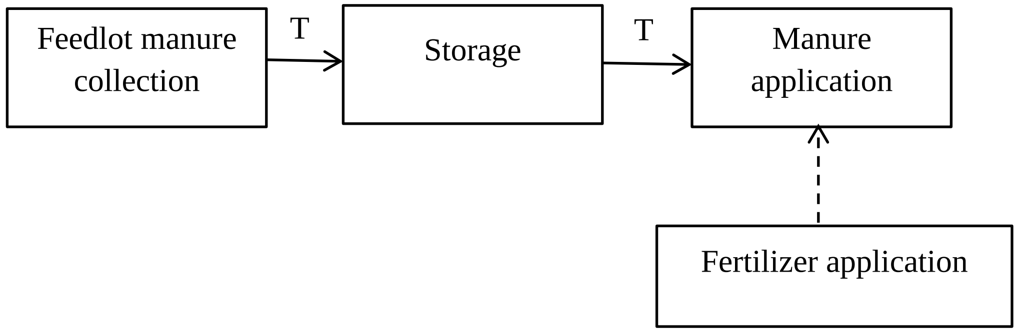

Figure 1. LCA boundary of land application system of feedlot manure (T stands for transportation and dashed arrows stand for avoided process)

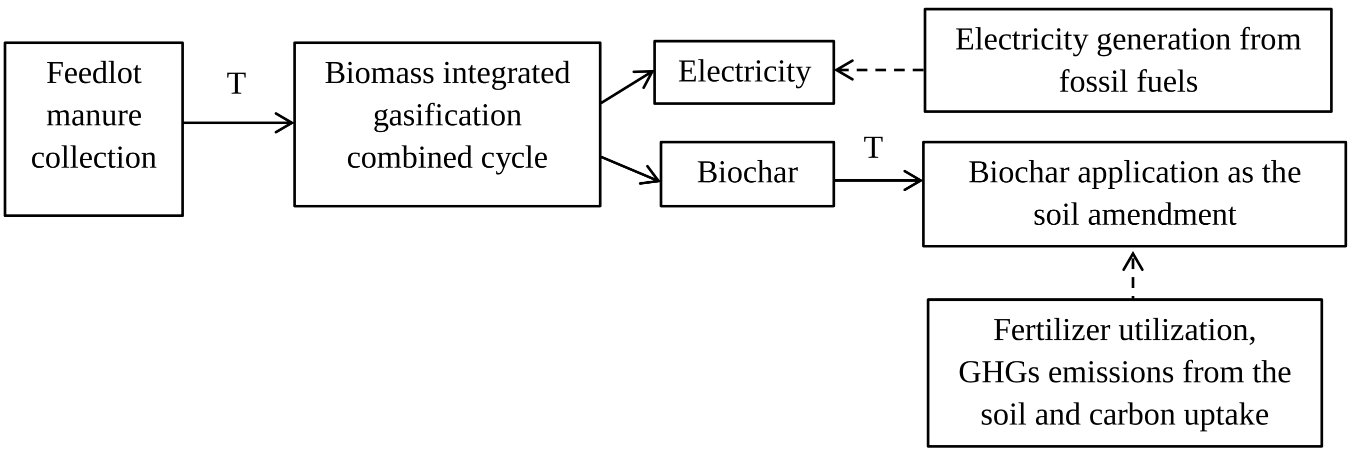

Figure 2. LCA boundary of gasification system of feedlot manure (T stands for transportation and dashed arrows stand for avoided process)

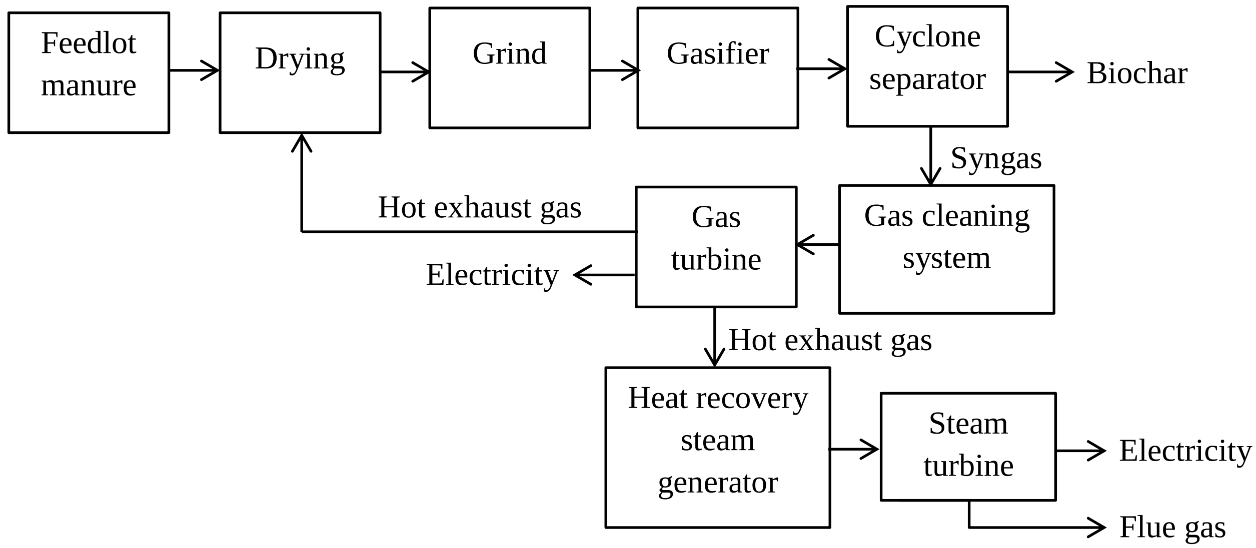

Figure 3. Schematic diagram of BIGCC system to process feedlot manure

CHAPTER VII

SUMMARY AND FUTURE RESEARCH RECOMMENDATIONS

In this dissertation, a comprehensive study was conducted to evaluate biomass gasification as an alternative solution to animal manure management, with the following major findings.

In chapter two, thermogravimetric analysis was used to examine the thermal behavior of dairy manure as a pyrolysis and combustion feedstock. Results revealed that thermochemical reactions were determined mainly by temperature, and heating rated influenced the start and the end of the conversions. The activation energies for the two major reaction zones were 93.63 kJ mol^{-1} and 84.53 kJ mol^{-1} for pyrolysis, and 83.03 kJ mol^{-1} and 55.65 kJ mol^{-1} for combustion.

In chapter three, we conducted an experimental study on dairy manure gasification on a fluidized-bed, laboratory-scale gasifier. Results showed that the increasing temperature increased the combustible gas and energy efficiency on the whole. In particular, an increasing steam to biomass ratio (0 to 0.8) led to a decreasing CH_4 concentration and an increasing H_2 concentration, and the declining ER (2.0 to 0) resulted in a rising concentration of CO. Also, the lower heating value of the syngas varied from 2.0 to 4.7 MJ m^{-3}, which could be combusted to generate heat and power.

In chapter four, feedlot manure was used as the feedstock to analyze the biomass gasification process. Results showed that energy efficiency was improved by higher temperature and equivalence ratio, but more steam injection caused a drop in energy efficiency due to the relatively lower temperature of the superheated steam. In addition, the optimum energy efficiency was 40%, when the temperature was 789 ^{o}C, equivalence ratio was 0.20, and steam to biomass ratio was 0.50.

In chapter five, effects of biochar from feedlot manure on nutrient leaching from two contrasting soils (clay and sandy loam soils) were examined. The conclusions were that biochar addition increased water holding capacity of both soils, and the higher the biochar addition rate was, the less leachate was collected. Also, BC1% (the addition of biochar to the soil at the rate of 1%) reduced cumulative NH_4^+-N by 5% and 19% for clay and sandy loam soils, respectively, however, biochar caused more P in the leachate during our experiment except for a temporary P reduction during the first leaching event. Therefore, more experimental data are needed before large scale application of biochar in agriculture.

In chapter six, life cycle assessment was used to evaluate greenhouse gas emissions during feedlot manure management systems (land application and gasification). Results showed that the net GHG emissions in land application scenario and gasification scenario were 119 and -643 kg CO_2-eq for one tonne dry feedlot manure, respectively. Consequently, it was concluded that gasification of feedlot manure is a potential technique to mitigate global warming effects.

Overall, biomass gasification, as an alternative solution to animal waste management, not only produces renewable energy, but also addresses some environmental issues caused by land application. In addition, the application of biochar from animal waste to the agriculture system has the potential to replace commercial fertilizer and reduce greenhouse gas emissions. However, the research and data about animal waste gasification is still limited, much more work should be suggested before its large scale application.

Based on the results of this dissertation, recommendations for future research include the following.

In chapter two, thermogravimetric analysis was used to examine the thermal behavior of dairy manure. However, the guidance of this knowledge to the design and optimization of thermochemical conversion units could be discussed.

In chapter three and four, dairy manure and feedlot manure were used as raw material for gasification. To strengthen the research on animal waste gasification, other possible materials, for instance, chicken litter and swim manure, could be uses as gasification feedstocks.

In chapter five, biochar effects on nutrient leaching was investigated during a three month experiment. However, physical properties of biochar, such as surface area and surface charge, could be analyzed to better explain the result. Also, a long term leaching experiment is recommended.

In chapter six, gasification system was compared to land application system in terms of greenhouse gas emissions. However, further comparisons among other alternative manure management solutions, like anaerobic digestion and composting, should be made. Besides that, the net energy for each manure management system should be estimated by life cycle assessment.